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DETACH SHEET BY CUTTING ALONG THIS LINE—PUNCH HOLES AND REINFORCE WITH GUMMED LINEN REINFORCEMENTS

12. GROUP I. THE ALKALI METALS. THE COPPER GROUP

A. GENERAL CONTRASTS

*12-1 Balance: 1 lb. Na in one pan with 1 lb. Cu in other. **Discuss relative densities in terms of ion size.**

12-2 Copper wire; K in CCl_4 in test tube over burner. **Melt Cu wire in burner; melt the K by heating CCl_4. Discuss relative melting points in terms of ion size.**

12-3 Large block Na, sodium press, wires from doorbell and battery. **Show conductivity, ductility.**

12-4 *Reactivity.* Na, K, penny, dime, forceps, knife, filter paper, 10 cm. crystallizing dish of water. **Cut small pieces of Na and K, blot clean, throw upon water (see 3-3). Compare with throwing coins into water.**

12-5 *Flame tests.* Shakers containing chlorides of Li, Na, K, Cu; burner. **Shake salts into flame showing color tests.**

12-6 *Stability of salts.* Na flakes, sticks, pellets; NaOH-aq., Na_2CO_3-aq., $AgNO_3$-aq., $CuSO_4$-aq.; four 400 ml. beakers, burner. **Form hydroxides and carbonates of Ag and Cu; show AgOH forms Ag_2O at room temperature, $Cu(OH)_2$ when heated forms black CuO; contrast with Na salts.**

B. THE ALKALI METALS. Li, Na, K, Rb, Cs, Fr

12-7 *General.* Exhibit lye, rubber, rayon, soap, etc.; NaOH pellets, flakes, sticks; KOH, KCl, washing soda, baking soda.

Sodium

*12-8 *Solvay process.* Conc. NH_4OH saturated with NaCl in 250 ml. wide-mouth bottle; dry ice. **Drop in chunks of dry ice, showing $NaHCO_3$ precipitating, Solvay process.**

Potassium

*12-9 *Gunpowder.* Mixture of equal volumes of KNO_3, charcoal and sulfur. Commercial gunpowder. **Contrast burning rate of synthetic mixture and commercial gunpowder (CARE).**

12-10 KNO_3 half-filling 5 cm. porcelain dish over Fischer burner; powdered charcoal, spoon. **When molten KNO_3 is very hot, sift in charcoal. CARE. Note purple flame *produced by K*.**

Cesium

12-11 Cesium photoelectric cell set up to ring bell.

Ammonium radical

12-12 NH_4Cl, NaOH, mortar and pestle, litmus paper. **Grind solids, show NH_3 off: smell, test with moist litmus paper.**

12-13 A 500 ml. Erlenmeyer flask containing 10 g. NH_4Cl + 10 g. NaOH + 20 ml. water; delivery tube leading into 1-liter beaker of water with few drops phenolphthalein indicator. **Show NH_3 bubbles off, coloring phenolphthalein red. Water sucks back into flask at end of experiment. Why?**

C. THE COPPER GROUP. Cu, Ag, Au

12-14 **Exhibit:** ores of these metals, finished products, coins, alloys, etc.

Copper

12-15 $CuSO_4$-aq., electrolysis apparatus. See 11-13 and 11-14.

12-16 $CuSO_4$ anhydrous; $CuSO_4$, $5H_2O$; wash-bottle, filter paper. **Sprinkle anhydrous powder on filter paper, then spray with water; blue $CuSO_4$, $5H_2O$ forms.**

Turn the page for additional demonstrations

*Footnotes

12-1 The pound block of Na can be stored indefinitely in a desiccator.

12-8 $NaCl + NH_3 + H_2O + CO_2 \rightarrow NaHCO_3 + NH_4Cl$. Solvay, the son of a salt merchant, lived as a boy with his uncle near a coal-tar works (NH_3 by-product) breathed out some CO_2 and perspired H_2O; he put all of his experiences together and got baking soda! Upon heating this he made washing soda: $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$.

12-9 Gunpowder is dangerous. Do not store in kit. Do not ignite it if tightly packed since it detonates explosively. Loosely pile no more than a gram of it, and set fire to it. It burns in a single flash, since it is properly granulated to give fast burning reaction; your synthetic mixture will burn much more slowly.

12-18 Indicate that the Fehling's test is used to detect reducing sugars in the urine; diabetics cannot assimilate the sugar.

12-22 A humorous twist can be given by dropping a dime (unknown to the students) into the AgCl precipitate; when the AgCl dissolves, the photographer's hypo (the sodium thiosulfate) dissolves the AgCl but not the Ag, so the dime suddenly flashes into view.

Labels for Topic 12. (For code, see instructions for assembling kits, J. Chem. Educ., **32**, 12A(1955).) 12-1-*J*-1-lb. Cu, 12-2-*w*-Cu wire, 12-2-*N*-CCl_4, 12-4-*w*-pennies, 12-4-*w* dimes, 12-5-*w*-shaker top-$LiCl_3$, 12-5-*w*-shaker top-NaCl, 12-5-*w*-shaker top KCl, 12-5-*w*-shaker top $CuCl_2$, 12-6-*J*-Na flakes, pellets, sticks, 12-6-*N*-NaOH aq., 12-6-*N*-Na_2CO_3 aq., 12-6-*N*-$AgNO_3$, 12-6-*N*-$CuSO_4$, 12-8-*N*-conc. NH_4OH, 12-8-*N*-sat. NaCl aq., 12-9-*w*-KNO_3, 12-9-*w*-charcoal, 12-9-*w*-sulfur, 12-10-*J*-KNO_3, 12-10-*J*-charcoal, 12-12-*w*-NH_4Cl, 12-12-*w*-NaOH, 12-13-*w*-NH_4Cl, 12-13-*w*-NaOH pellets, 12-13-*d*-phenolphthalein soln., 12-15-*N*-$CuSO_4$ aq., 12-16-*w*-$CuSO_4$ anhydrous, 12-16-*w*-$CuSO_4$, $5H_2O$, 12-17-*N*-$CuSO_4$ aq., 12-17-*N*-NH_4OH, 12-18-*Stock, Fehling's Solution A:* 69 g. $CuSO_4$ $5H_2O$ + 1000 ml. water, 12-18-*Stock, Fehling's Solution B:* 350 g. Rochelle salt (NaK tartrate) + 100 g. NaOH + 1000 ml. water, 12-18-*N*-Fehling's solution A, refill from stock, 12-18-*N*-Fehling's solution B, refill from stock, 12-18-*N*-sucrose aq., 12-18-*N*-glucose aq., 12-19-*Stock, Silvering solution A:* 10 g. $AgNO_3$ + 500 ml. water, + NH_4OH till precipitate dissolves + 500 ml. water more, 12-19-*Stock, Silvering solution B:* 2 g. $AgNO_3$ + 1.6℄ g. Rochelle salt (NaK tartrate) + 1000 ml. water, 12-19-*N*-silvering solution A, refill from stock, 12-19-*N*-silvering solution B, refill from stock, 12-20-*d*-$K_2Cr_2O_7$ aq., 12-20-*N*-$AgNO_3$ aq., 12-20-*d*-Na_2AsO_4 aq., 12-20-*d*-KCl aq., 12-20-*d*-KBr aq., 12-20-*d*-KI aq., 12-21-*d*-$AgNO_3$ aq., 12-21-*N*-NaCl aq., 12-21-*w*-Mg ribbon, 12-22-*w*-dimes, 12-22-*d*-$AgNO_3$ aq., 12-22-*d*-NaCl aq., 12-22-*N*-sodium thiosulfate aq., 12-23-*w*-gold leaf, 12-24-*N*-blue colloidal gold, 12-24-*N* red colloidal gold, 12-24-*d*-gold chloride dilute solution.

DETACH SHEET BY CUTTING ALONG THIS LINE—PUNCH HOLES AND REINFORCE WITH GUMMED LINEN REINFORCEMENTS

12-17 *Cupric tetra-ammine.* $CuSO_4$-aq., NH_4OH, two 2-liter jars. **In one jar add NH_4OH to 20 ml. $CuSO_4$-aq. in water, forming $Cu(OH)_2$. In the other repeat this, then continue to add more NH_4OH to form deep purple $Cu(NH_3)_4SO_4$.**

*12-18 *Fehling's Test.* Solution A: 69 g. $CuSO_4$, $5H_2O$ in 1000 ml. water. Solution B: 350 g. Rochelle salt (NaK tartrate) + 100 g. NaOH + 1000 ml. water. Two 250 ml. beakers over burners, sucrose-aq., glucose-aq. **In one beaker heat 100 ml. solution A + 100 ml. solution B + 10 ml. glucose-aq.; in the other use A + B + 10 ml. sucrose-aq. The first, being a reducing sugar, reduces Cu^{++}, a color change from blue to green to yellow to red (Cu_2O) occurring. Nothing occurs with sucrose.**

Silver

12-19 *Silver mirror.* Solution A: 10 g. $AgNO_3$ in 500 ml. water. To this, add NH_4OH until the precipitate which first forms dissolves, then add 500 ml. more water. Solution B: 2 g. $AgNO_3$ + 1.66 g. Rochelle salt (NaK tartrate) + 1000 ml. water. A 500 ml. Ernlenmeyer flask over burner. **Mix equal quantities of solutions A and B, warming if necessary; silver mirror forms in few minutes.**

12-20 *Insoluble silver salts.* $AgNO_3$-aq., $K_2Cr_2O_7$-aq., Na_3AsO_4-aq., KCl-aq., KBr-aq., KI-aq., six test tubes. **Form silver salts.**

12-21 *Photographic process.* Unexposed photographic film, a negative and a positive film, $AgNO_3$-aq., NaCl-aq., filter paper, funnel and filter stand, Mg ribbon, burner, forceps. **Form AgCl; filter; blot precipitate dry, spread on filter paper. Expose half of it to the light of a burning Mg ribbon; dark Ag forms, as in photographic process.**

*12-22 *Photographic fixer action.* Dime, $AgNO_3$-aq., NaCl-aq., sodium thiosulfate-aq., a 400 ml. beaker. **Form AgCl then add sodium thiosulfate, stirring; this dissolves the AgCl imitating the operation of photographic fixing.**

Gold

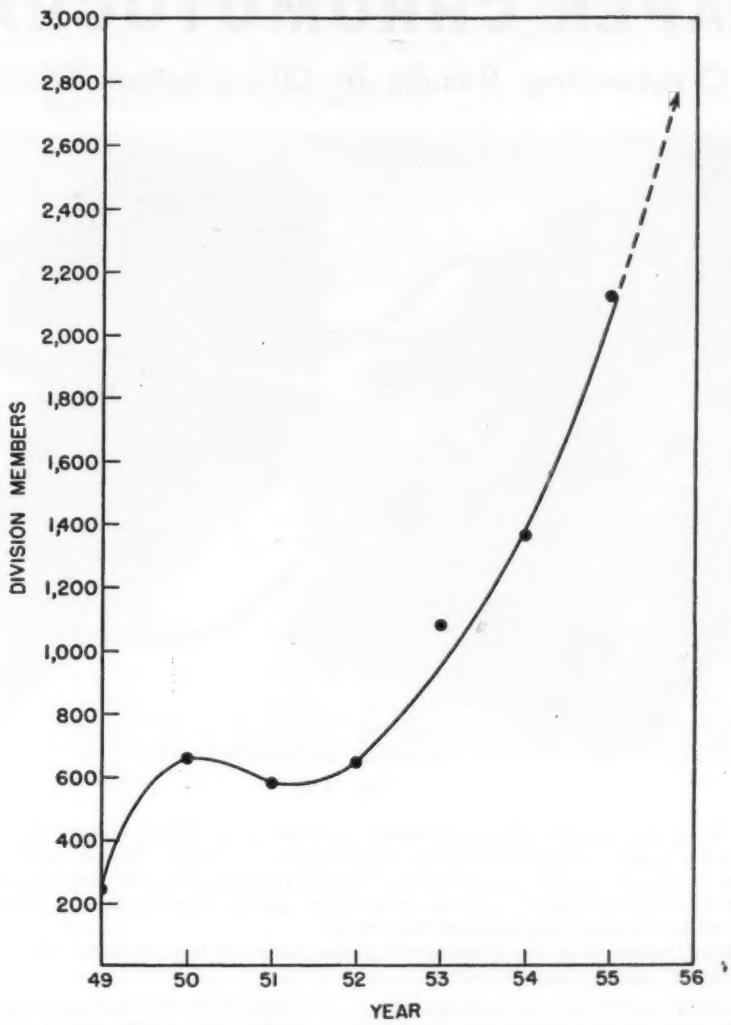
12-23 Gold leaf, conc. HNO_3, conc. HCl, test tubes. **Dissolve gold in aqua regia (1 volume HNO_3 + 3 vols. HCl).**

12-24 **Exhibit:** red and blue varieties of colloidal gold; gold chloride-aq.

Next month's Tested Demonstrations in General Chemistry

13. GROUP II. THE ALKALINE EARTH METALS. THE ZINC GROUP

For a complete list of topics for 1955–6 see J. Chem. Educ., 32, 28–9(1955)



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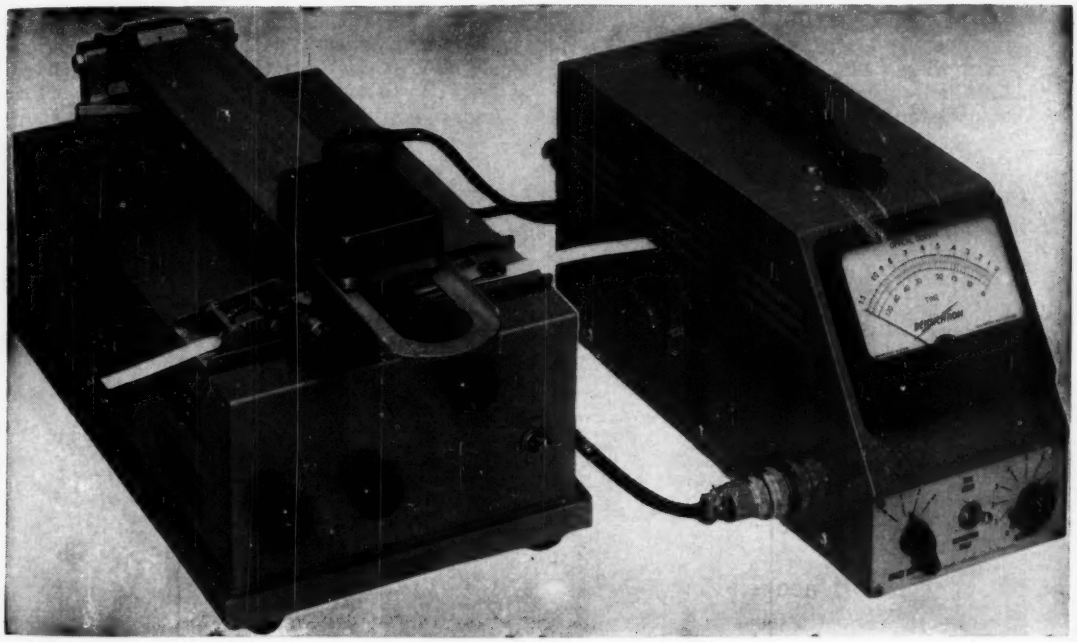

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Editor's Outlook

DECEMBER is a month when thoughts often rise above the usual level of the year's activity. Not only does the end of the year encourage retrospect, but almost always there are times during the hectic mechanical idolatry of the Christmas season when men's minds are drawn to the contemplation of some larger meanings in the flow of the world's events. When we think of the big events in science for 1955, we are reminded of Pasteur's words. He referred to himself as "... a man whose invincible belief is that science and peace will triumph over ignorance and war, that nations will unite, not to destroy but to build, and that the future will belong to those who will have done most for suffering humanity."

Here is a credo for the thoughtful scientist. Unhappily, it sometimes has been the bland idealist chirping the happy song of the inevitability of progress who has taken over such high-sounding words and cheapened their meaning. Realistically, humanity is still suffering. Science has not worked itself out of a job by attaining that goal of triumphant ascendency over ignorance and war. Nevertheless, as 1955 joins history's parade of the years, a contemplative scientist thinking about his colleagues' achievements can make an interesting list. It will contain events with more genuinely optimistic implications than has been the case in some recent years. What are some of these events? We shall suggest only two.

The unparalleled success of the Geneva "Atoms-for-Peace" Conference probably heads any list. In spite of the S in UNESCO, the repeated statements-of-position by eminent scientists, and even the Eisenhower proposal of December, 1953, the man in the street still has located chemistry and physics in the camp of the destroyers of humanity. Even more wrong has been the layman who put the chemists and the physicists themselves on the same shelf with the A bomb, H bomb, and C bomb. Here they were to be tucked away until the time when some mysterious, soulless super-scientist should decide to do away with humanity. The dramatic demonstration of exactly the opposite point of view at Geneva makes that meeting science's most historically-significant Christmas present to humanity in 1955. Science once again appears to the layman to be the activity engaged in by world citizens. A technical meeting is supposed to advance knowledge by allowing for exchange of research information and the airing of new hypotheses. The profound effects this meeting had on international relations may prove to be even more significant than its advancement of nuclear science. The forces of freedom as well as the forces for unity in our mid-twentieth century world are stronger as a result.

A second event of the year belongs on any list of this type. We refer to the Salk-vaccine experiment. Opinions may vary on its administration, its timeliness, or the degree to which it was more than an "experiment." That it is one more way in which science has "strengthened the hand of the Good Samaritan," few will deny. Beyond this rather obvious significance there seems to us to be an aspect of great importance to the understanding of science by the humanity it serves. This is the greater appreciation of the statistical nature of much of our scientific knowledge. The reverence of the layman for the laws of physical science is often coupled with a false hope for the time when society can apply the allegedly all-powerful scientific method and discover equally valid laws for itself, analogous to those for molecules. Nothing tempers the worship of statistics like being a statistic. Being even a statistical victim of polio is not to be taken lightly. In this setting the people participating in the experiment, while realizing that they represent a large portion of the population, still think of themselves as individuals. This experience should lead to a more realistic appreciation by laymen of the statistical nature of many of science's laws. Perhaps the acceptance of one more misconception thus can be lessened.

These are but two of the year's events which can make this Christmas certainly more peaceful and possibly less ignorant. In each, science has done more than reveal new information. "Knowledge comes, but wisdom lingers," said the poet. We would like to think that in 1955 science has sped the laggard just a little.

AROMATIC SUBSTITUTION BY FREE RADICALS

PETER F. NELSON
Royal Melbourne Technical College,
Victoria, Australia

ALTHOUGH electrophilic and nucleophilic aromatic substitution have been treated extensively in recent texts and review articles (*1*), homolytic substitution has received relatively little attention. An attempt is made here to summarize recent investigations upon orientation and reaction rates.

EARLY WORK

The various early reports of aromatic radical substitution must be treated with caution, since quantitative data is usually lacking. Solubility differences made strict comparison of yields difficult, and in many cases only the principal products were isolated. Although the Gomberg reaction had been established as a method of arylation since about 1924, the first recorded example of the isolation of all three isomers in a homolytic arylation process (*2*) did not appear until ten years later.

Nevertheless, in the period from 1930 to 1950 it became clear that in radical reactions the usual rules of orientation were not observed, and that substitution frequently took place para and ortho to the original substituent, irrespective of whether it was normally classified as para-ortho or meta directing.

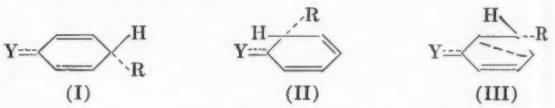
In 1938–39, Hey (*3*) obtained approximate figures for the isomer distributions observed when chlorobenzene, bromobenzene, and toluene were substituted by the diphenyl radical, which pointed definitely to para-ortho orientation. Some ten years later a somewhat similar picture emerged from the work of Loebl, Stein, and Weiss on the hydroxylation of nitrobenzene (*4*).

Much of the earlier work involved the separation of reaction products and the value of the results was therefore markedly dependent on the separation techniques. It is not surprising that the less soluble para compounds were often isolated in higher yield than the generally more soluble ortho isomers, a fact which led to underestimation of the extent of ortho substitution. The last few years have seen the application of more rigorous analytical methods which do not require separation of the products at all, particularly infrared spectroscopy. Although earlier semiquantitative reports are discussed, it is chiefly with the more recent accurate results that this paper is concerned.

THEORY OF AROMATIC HOMOLYTIC SUBSTITUTION

Since in homolytic substitutions the attacking entity usually carries zero charge, it might be expected that the reaction would not be susceptible to directive influences due to substituents. If this were so, the ratios of isomers produced would be 40 per cent ortho, 40 per cent meta, and 20 per cent para. Since substitution is found to be predominantly para-ortho (*i. e.*, meta < 40 per cent), substituents evidently do exert a directive effect.

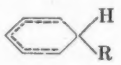
As in many cases of activation toward electrophilic reagents, activating groups usually activate all positions, but the predominance of para and ortho substituted products may be understood from a consideration of the transition states for substitution of Ph—Y by radical R (*5*).



(I) (II) (III)

Evidently the energy of structures (I) and (II) should be lower than that of (III), since the conjugation is less complete in the latter case.

The transition state in radical substitution of benzene presumably involves the formation of a pentadienyl radical, which, since it may be considered as derived from either a pentadienyl cation or anion, ought to be stabilized by substituents which will stabilize either the cation or the anion (*6*). Thus, formation of the



transition state should be facilitated by both electron-yielding and electron-withdrawing substituents. Quantum-mechanical studies by Wheland and Coulson lead to similar conclusions (*7*, *8*).

The fate of the H atom which is lost from the transition state, presumably at the position of substitution, is uncertain. It may produce new radicals, or it may reduce either reactants or products.

It must be remembered that substitution is not the only possible mode of attack by radicals on aromatic systems. Abstraction of hydrogen may also take place with the production of aromatic radicals:

$$\mathrm{Ar{-}H + R\cdot \longrightarrow Ar\cdot + RH}$$

and these would be expected to yield diaryls by dimerization.

$$\mathrm{Ar\cdot + Ar\cdot \longrightarrow Ar{-}Ar}$$

Although abstraction of hydrogen has been found to

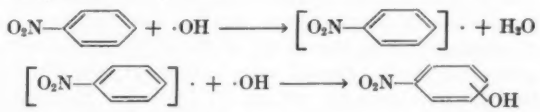
occur in some reactions, disubstituted derivatives of diphenyl are not found as products of the phenylation of monosubstituted benzenes (*9*).

The reactivity of organic radicals varies considerably; in general, alkyl radicals do not react with benzene derivatives unless the latter are highly activated. In most investigations the organic radicals have been aromatic.

ORIENTATION BY SUBSTITUENTS

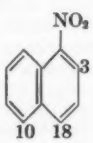
Nitro Group. Substitution of nitrobenzene has been extensively studied (*5*, *10*, *11*), especially by Hey and co-workers. Attack by phenyl and substituted phenyl radicals is effective at all positions in the nucleus, and para-ortho orientation is the rule; phenyl radicals from five different sources yield substantially the same isomer distribution. Quantitative data for this and other reactions are given in Table 1. Analyses were carried out both by bromometric titration of the bases obtained on reduction of the nitrodiphenyls, and by infrared spectroscopy.

All three mononitrophenols are produced by attack of hydroxyl radicals on nitrobenzene, but the proportion of meta isomer is substantially less than the "statistical" 40 per cent. Loebl, Stein, and Weiss have used Fenton's reagent (*4*) and the action of X-rays on aqueous solutions (*12*) as radical sources. Although the two methods appear to yield similar results, side-reactions made it difficult to obtain any but approximate figures with Fenton's reagent, and only the results with X-rays are included in Table 1. Isomer proportions were found to vary somewhat with changing pH. The reactions proceeded readily in the cold, and were formulated:



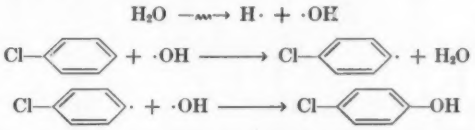
As might be expected, large quantities of dinitrodiphenyls were formed in addition to the three nitrophenols. It is noteworthy that some attack took place at the 1-position, the nitro group being removed by a hydroxyl radical to give a phenyl radical and nitric acid.

Approximate figures were reported by Dannley and Gippin (*13*) for benzoyloxylation of 1-nitronaphthalene using benzoyl peroxide. Substitution occurred in the 2-, 4-, and 5-positions, the mole ratios of isomers being as shown:



Halogens. Substitution of chlorobenzene by hydroxyl radicals produced by X-rays has been shown to yield less than 40 per cent of the meta isomer, though the figures cited are approximate (*14*). The isomer distribution was found to vary with changing pH of the reaction medium, the percentage of meta isomer being higher at pH 2 than at pH 6 or 12. Similar results attended the use of Fenton's reagent.

The authors formulated the hydroxylation reaction as follows:



Phenyl radicals attack the halobenzenes in all three positions, the isomer distribution being similar for all four compounds (*15*, *16*). The percentage of ortho isomer is roughly the same as in the phenylation of nitrobenzene, but the figures for meta and para isomers are quite dissimilar. In the case of the halogen compounds the percentage of meta isomer is approximately three to four times as great as that found for nitrobenzene, while the percentage of para isomer is about half as great. The ratio of meta to para halodiphenyls is roughly 2:1, *i. e.*, the "statistical" ratio.

When attached to a naphthalene nucleus, chlorine and bromine direct benzoyloxy radicals mainly into the 4- and 5-positions, but some 2- isomer is also formed (*13*). The mole ratios of the various isomers are as indicated.

Hydroxyl groups. Like nitrobenzene, phenol is readily substituted by hydroxyl radicals derived from Fenton's reagent or from the action of X-rays on aqueous solutions (*17*).

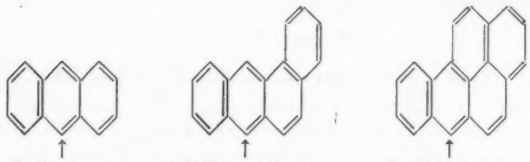
Oxidation and complex formation occur when ferric ions are present, and the X-ray method has proved more amenable to quantitative study. Quinol and catechol are both formed, but not resorcinol. The ratio of quinol to catechol varies with changing pH, but is about two in neutral solution. Under some conditions quinones are produced, apparently without the intermediate formation of dihydroxy-benzenes. It is of interest that *o*-benzoquinone, the predominating quinone in acid solution, is also formed when *neutral* solutions of phenol are subjected to the action of tyrosinase.

Hydrocarbons. Aromatic hydrocarbons other than benzene present a problem in orientation, but quantitative information concerning radical substitution in such molecules is rather meager.

Naphthalene yields 1- and 2-naphthols when treated with benzoyl peroxide, Fenton's reagent, or solutions of hydrogen peroxide irradiated with ultraviolet light (*18*). The ratio of 1- to 2-naphthol formed in the two

latter reactions has been estimated from paper chromatograms as approximately three or four to one. The formation of salicyclic acid also was observed.

The most reactive positions for attack by benzoyloxy radicals in solvent chlorobenzene at 80°C. have been studied for a number of polycyclic aromatic hydrocarbons (*19*). These positions are indicated by arrows in the formulas below. Phenanthrene and chrysene



Anthracene 1,2-Benzanthracene 3,4-Benzopyrene

are inert under these conditions. There is a low yield of dibenzanthraquinones when 1,2-5,6-dibenzanthracene reacts in the presence of air.

Diphenyl is substituted by phenyl radicals in all three positions, the ortho isomer comprising about 50 per cent of the total (*20*). The percentage of para isomer is slightly greater than that of meta.

Two examples of the orientating effect of an aliphatic side chain recently have been studied by Hey and co-workers. The compounds chosen, toluene and *tert*-butyl benzene, present a striking contrast. Phenylation of toluene[1] results in a yield of *o*-methyl diphenyl of approximately 71 per cent, with the yield of meta compound somewhat greater than that of the para (*21*). *Tert*-butyl benzene, on the other hand, yields only 24 per cent of *o-tert*-butyldiphenyl, with the meta and para isomers in approximately statistical ratio (*22*). As can be seen from Table 1, the ortho isomer invariably accounts for at least half the total product in other aromatic phenylations, and the low yield of *o-tert*-butyldiphenyl is ascribed to steric hindrance. It is interesting that the other examples of homolytic substitutions in which the yield of ortho isomer is well below 50 per cent are the hydroxylation of nitrobenzene and chlorobenzene.

Heterocycles. Little quantitative information is available concerning radical substitutions in heterocycles. It recently has been shown that pyridine is phenylated at all positions, but more than 50 per cent of the product is 2-phenyl pyridine (*23*). The ratio of meta to para isomer is statistical, *i. e.*, 2:1.

Recent work has shown that quinoline is nitrated by pernitrous acid in the 6- and 7-positions, *i. e.*, in the benzenoid ring (*24*). This reaction is believed to involve both hydroxyl and nitrogen dioxide radicals, and is of interest since the reactivity of benzene and pyridine toward phenyl radicals is about equal. There is apparently no formation of 5- and 8-nitroquinolines.

REACTION RATES

The problem of reaction rate is closely connected with that of orientation. The division into para-ortho- and meta-directing substituents is much less definite for homolytic substitution than for many heterolytic reactions, and this blurring of familiar distinctions applies equally well to the rates of homolytic substitution reactions. The enormous changes in rate which frequently accompany change of substituent in heterolytic substitutions have not been observed in corresponding homolytic reactions.

Two main approaches are available for the study of the effect of substituents on reaction rates. The first is the direct measurement of rate constants with and without the substituent. This method involves the difficulty that in many cases there is no certainty that the rate-determining stage is the substitution itself. The second method, that of competitive reaction, consists in allowing an equimolar mixture of two compounds under comparison to compete for a limited quantity of reactant. The latter approach has proved the more useful in the study of both heterolytic and homolytic substitution. An extension of the method allows indirect comparison of rates for two compounds which cannot be compared directly (*25*).

One of the first experiments of the competition type to yield useful information was that of Grieve and Hey (*26*), who observed that the yield of nitrodiphenyls was four times as great as the yield of methyl diphenyls when toluene and nitrobenzene were allowed to compete for phenyl radicals. Eighteen years later, Hey and co-workers obtained a quantitative comparison of the rates of substitution of benzene, nitrobenzene, chlorobenzene, and pyridine by phenyl radicals (*9*). The relative rates are as shown in parentheses:

$$PhH\ (1);\ PyH\ (1);\ PhCl\ (1.44);\ PhNO_2\ (4)$$

Since the isomer proportions are known for the phenylation of nitrobenzene, partial rate factors[2] can be calculated, and the effect of the nitro group completely specified. Partial rate factors for this and for other phenylations are set out in Table 2. Evidently the nitro group weakly activates all positions, but chiefly the ortho and para. These results agree qualitatively with theoretical predictions (*7*).

A similar investigation has been carried out with chlorobenzene (*15*), and the partial rate factors (Table 2) show that the ortho position is activated to the greatest extent, the para position only slightly, while the meta position is scarely more reactive than benzene itself. The over-all rate of substitution is 1.44 (benzene = 1), so that the nitro group activates about three times more powerfully than does the chlorine atom.

[1] Substitution in the side chain may also occur, but can be eliminated by using a low concentration of benzoyl peroxide.

[2] The partial rate factor for a given position in a given reaction is the numerical value of the reactivity of that position compared to the reactivity of a position in benzene in the same reaction, the latter having the value unity. The partial rate factor incorporates the statistical fact that there are six equivalent positions in benzene, and two equivalent ortho and two equivalent meta positions in a monosubstituted benzene. A partial rate factor greater than unity means activation, a partial rate factor less than unity means deactivation. The over-all rate of a reaction relative to benzene is obtained by adding the partial rate factors for the five positions in a monosubstituted compound and dividing by six.

As in the nitrobenzene case, theoretical predictions are in qualitative agreement with experiment. The difference in activating influence of the nitro group and chlorine atom also has been demonstrated by Dannley and Gippin for the attack of benzoyloxy radicals (from benzoyl peroxide) on the α-substituted naphthalenes. The relative rates of substitution are shown in parentheses for the substituents studied (*13*).

NO_2 (19); Br (2.0); Cl (1.2); H (1.0)

It is interesting that the benzoyloxy and not the phenyl radical attacked the nucleus, indicating that naphthalene is more reactive in homolytic reactions than benzene. The same is true of anthracene, 1,2-benzanthracene, and 3,4-benzopyrene (*19*).

More recently partial rate factors have been obtained for substitution of fluoro-, bromo-, and iodobenzene by phenyl radicals (from benzoyl peroxide) (*16*). The values for nitrobenzene and the four halobenzenes are shown in Table 2.

It is evident that with all the halobenzenes except fluorobenzene the partial rate factors are in the order *o*-> *p*-> *m*-, and that every position is activated, even if only slightly. The halides thus present a picture similar to that for nitrobenzene, although the definite para-ortho orientation found with the latter compound is much less evident, the activating influence of the halogens being weaker and much more evenly distributed over the ring.

The over-all activating effect of the halogens varies in the order I > Br > Cl > F, which, as Hey, *et al.* (*16*), have remarked, differs from that observed in electrophilic substitution where the order is F > Cl > Br < I. The latter order is presumably due to competition between inductive electron attraction and conjugative repulsion, which both vary in the order F > Cl > Br > I. The undisturbed order found in homolytic substitution is considered by Hey, *et al.*, to demonstrate that the latter type of reaction is not susceptible to electrostatic influences on charge distribution in the aromatic molecule. Theoretical considerations based on free valence numbers (*27*) lead to predictions which are in qualitative agreement with experiment.

The rates of substitution of halobenzenes by phenyl radicals have recently been compared with the rate of substitution in pyridine (*23*). The values found were PhI (1.1) > PyH (1.0) > PhBr = PhCl (0.9) which differ somewhat from those reported previously (*15*, *16*). The authors point out that solvent association in the competition reaction makes it necessary to exercise caution in applying their relative reactivities to other solvent systems.

The fact that homolytic substitutions are susceptible to steric influences is illustrated by the partial rate factors for the reaction of phenyl radicals with *tert*-butylbenzene and *p*-di*tert*-butylbenzene (*22*) (Table 2). This is the first recorded case of over-all deactivation in homolytic aromatic substitution, and is attributed to steric hindrance by the *tert*-butyl group of the usually favored ortho position. Both the meta and para positions are activated. The partial rate factors for these positions are roughly comparable to those for fluorobenzene, and it is likely that the *tert*-butyl group would be activating in the absence of steric effects. Introduction of a second *tert*-butyl group into the para position further reduces the over-all rate, but the partial rate factor for the four equivalent (ortho) positions is raised, the reactivity being just less than that of benzene.

The steric effect of the *tert*-butyl group has been noticed in electrophilic substitutions; partial rate factors for mononitration of *tert*-butyl benzene are given in Table 3 (*28*). The inhibitory effect exerted by the *tert*-butyl group on substitution in the ortho position recently has led to its use as a protecting group in the synthesis of 1,2,3-trialkyl benzenes (*29*).

The effect of the methyl group is one of mild activation. The partial rate factors are in the order ortho > para > meta, showing the absence of steric influence (*21*). The reactivity of the meta position is the same as that of a position in benzene.

TABLE 1

Isomer Percentages in Homolytic Aromatic Substitution Reactions[a]

Reactant	*Radical*	*Source*	—*Orientation*, %— *o*-	*m*-	*p*-	*Ref.*
$PhNO_2$	Ph	various	58	10	33	(*5*)
"	"	"	65	4	31	(*11*)
"	"	$Pb(OBz)_4$	55	16	29	(*10*)
"	*p*-BrPh	various	..	12	..	(*5*)
"	*p*-CH_3Ph	"	..	9	..	(*5*)
"	OH	X-rays	33	29	39	(*12*)
PhF	Ph	Bz_2O_2	54	31	15	(*16*)
PhCl	"	Bz_2O_2 and Gomberg	62	24	14	(*15*)
"	OH	X-rays	15–40	20–35	35–60	(*14*)
PhBr	Ph	Bz_2O_2	49	33	17	(*16*)
PhI	"	"	52	32	17	(*16*)
Ph—Ph	"	"	49	23	29	(*20*)
Ph—CH_3	"	"	71	17	12	(*21*)
Ph-*t*-Bu	"	"	24	49	27	(*22*)
pyridine	"	"	58	28	14	(*23*)

[a] Unless otherwise indicated, figures given are mean value and are correct to the nearest integer.

TABLE 2

Partial Rate Factors for Phenylation of Substituted Benzenes

	NO_2	F	Cl	Br	I
	7.0 / 1.2	2.20 / 1.25	2.7 / 1.03	2.59 / 1.75	2.79 / 1.70
	7.9	1.20	1.2	1.83	1.80
Over-all rate	4.05	1.35	1.44	1.75	1.80

	CH_3	*t*-Bu	*t*-Bu
	4.1 / 1.0	0.63 / 1.28	0.93 / *t*-Bu
	1.4	1.41	
Over-all rate	1.9	0.87	0.63

SUMMARY

Owing largely to the work of Hey and his collaborators, a more or less clear picture of homolytic aromatic substitution has begun to emerge. The familiar division into para-ortho directing (activating) and meta directing (deactivating) groups, which holds reasonably well for many electrophilic substitutions (and in inverted form for nucleophilic substitutions), loses its significance when homolytic substitution is considered.

TABLE 3
Partial Rate Factors for Mononitration of Substituted Benzenes (*30*)

	Cl	Br	CH_3	*t*-Bu
	0.030 / 0.00	0.037 / 0.00	42 / 2.5	5.5 / 4.0
	0.139	0.106	58	75
Over all rate	0.033	0.030	24.5	15.7

It is evident from the foregoing survey that, with the exception of the *tert*-butyl group, all substituents so far investigated are para-ortho directing, but it is equally evident that the division into para-ortho orientation on the one hand and meta orientation on the other has lost much of its sharpness. Where the proportion of meta isomer is in the neighborhood of 30 per cent (*e. g.*, phenylation of halobenzenes), it seems almost appropriate to speak of an ortho-meta directing group. Indeed the term "para-ortho directing" retains its significance only in terms of the inequality $p- + o- > 60$ per cent.

This blurring of the distinctions applicable to heterolytic substitution applies with even greater force to reaction rates. In the first place, all groups so far investigated, with the exception of *tert*-butyl, are activating, and the ortho position is usually more reactive than the others. Secondly, the effect of a substituent is generally small compared with the effect of the same substituent in a heterolytic reaction. The introduction of a nitro group into the benzene ring may reduce the rate of electrophilic substitution by a factor of about 10^4; the same change may increase the rate of homolytic substitution a mere fourfold. Partial rate factors for some electrophilic substitutions (nitration) are given in Table 3 for comparison with those for the corresponding phenylations.

The polar character of substituents does not appear to influence activation to any great extent. It may be argued that electron-attracting substituents should activate more strongly than electron donors (*6*). While the evidence available is as yet insufficient to test this conclusion, it is interesting that the nitro group is certainly a more powerful activator than the halogens.

The lack of any marked dependence of activation on polarity is hardly surprising, since the neutral attacking reagent should be uninfluenced by permanent electrostatic charges in the substrate molecule, and should also be unable to induce charge drift of the conjugative type. There is, however, some indication that reactivity may be related to the length of the conjugated system in aromatic molecules (*30*), since reactivity increases in the order:

$$PhH \approx PyH < PhCl < PhNO_2 <$$ naphthalene, phenanthrene, etc.

Theoretical treatments of the reactivity of aromatic systems toward free radicals have yielded results which agree qualitatively with experiment. The predicted efforts are in the right direction and of the correct order of magnitude, though usually somewhat high. The agreement must be regarded as encouraging.

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GEOLOGY AS A PART OF THE COLLEGE GENERAL CHEMISTRY COURSE

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IT HAS been the experience of many a science student that the more he delves into his own special field, the more he senses its ramifications in other areas of science. In an article on the California Institute of Technology, in *Time*,[1] we note:

> . . . the old compartments of knowledge no longer have their old rigid meanings. At Caltech it is possible to find a top geologist, *e. g.*, Harrison Brown, who has never taken a formal course in geology. It is not only possible, but standard operating procedure for the scholars of Caltech to invade each other's fields as if no walls had ever existed between them at all. "Nature," says Physicist Bacher, "is not physics or chemistry or biology. It is all three—and much more besides." As one alumnus put it to Scholar Hallett Smith: "When I was an undergraduate, I majored in biology. But, of course, Caltech's biology is really biochemistry. Now everybody knows that chemistry is only a branch of physics, but it took me until my senior year to realize that physics is a branch of philosophy."

Apparently the traditional subject delineations are arbitrary; to call this phase of our observation of natural laws "physics" and that phase "chemistry" is no more divinely ordained than to designate this segment of time as "nine o'clock" and that as "Tuesday."

Chemistry is often classified as a "natural science," yet the student's sole experiences may be with neatly bottled c. p. substances which are far removed from their natural origin, or even synthesized by man. The story is told of a college senior, "who, when asked to name the sources of potassium compounds, replied, 'There are three sources—Merck, Baker, and Mallinckrodt.' "[2]

Since the scope of chemistry as a science is what man chooses to define, it seems that more study of the "natural" forms of matter and the changes which it undergoes *in nature* is in order. This, then, is a plea for more "geochemistry" in a general chemistry course—for a closer integration of geological science and chemistry.

Chemistry textbooks of necessity carry some slight reference to geological terms and concepts. The natural occurrence of elements, minerals, ores, and salts is usually given, with occasional illustrations of mineral crystals, ore deposits, limestone caves, etc. Perhaps the area in which the chemistry texts lean most heavily on geology is that of physical and chemical properties in relation to molecular structure. The section on silicates in a recent textbook[3] illustrates the possibilities in this area. Ring-structure silicates (beryl, emerald) are pictured and explained. Silicate chains are illustrated by pyroxenes and amphibole (tremolite or chrysostile—"asbestos"), with the explanation that it is hard to cut across the chains, but the materials are readily shredded into fibers by cleavage of their crystals along the axis in which the chains lie. Layer structures are also discussed. Then[4]:

> In talc, $Mg_3Si_4O_{10}(OH)_2$, the silicate layers are alternated with layers of magnesium and hydroxide ions. Each pair of layers is electrically neutral and is loosely bound to the layers above and below it. As a result, the layers readily slide past each other when a crystal of talc is subjected to slight pressure. The properties of softness and smoothness for which talc is valued are direct consequences of its crystal structure.

Further discussions of mica, feldspar, and quartz are encountered. It is apparent here that actual examination of specimens such as beryl, quartz, talc, mica, and feldspar is desirable if the words of the text are to be visualized by the student.

And why not have rock and mineral specimens as a part of chemistry teaching equipment? Admittedly, we would prefer that the student, somewhere in his general science background, should have learned enough about rocks and minerals to recognize mica and quartz; but even if he does not have a good background in earth science, here is a fine opportunity to make chemistry more concrete and meaningful.

Beyond mere use of rock and mineral specimens as "visual aids" in chemistry, and occasional reference to occurrence in nature of elements and compounds, what are some areas in which geology might be given more of a place in general chemistry than it is at present?

(1) Physical and chemical properties of matter in relation to molecular structure are most apparent in natural mineral specimens. Dr. Linus Pauling, in speaking before the Sixth Conference on the Teaching of Chemistry at Fisk University, June 15, 1955, said: "Take advantage [in your teaching] of the knowledge of the structure of giant molecules"; and then he illustrated the close relationship between structure and properties in the silicates—the long chains of asbestos, the mica planes, and a different structure again in talc. "The way in which atoms are held together by bonds expresses itself clearly in properties." How a textbook may develop this idea has already been indicated.

(2) The concept of chemical change as a natural phenomenon rather than as merely a test tube reaction may be strengthened by reference to geology. Chemi-

[1] *Time*, LXV, No. 20, 79 (May 16, 1955).

[2] FLEISCHER, MICHAEL, "The abundance and distribution of the chemical elements in the earth's crust," J. CHEM. EDUC., 31, 446 (1954).

[3] MARKHAM, EDWIN C., AND SHERMAN E. SMITH, "General Chemistry," Houghton Mifflin Co., Boston, 1955.

[4] *Ibid.*, p. 493.

cal changes are often very dramatic in the outdoors; the action of the atmospheric oxygen, carbon dioxide, and moisture on the rocks ("chemical weathering") to change their color, composition, and eventually to crumble them to clays and soils is a fascinating area to explore. Whence the stalactites and stalagmites in caves? Why do some rocks disintegrate faster than others? Why do freshly broken rock surfaces change color after a while? Considerable chemistry is required in finding the answers to questions like these, which involve dynamic processes in nature's laboratories.

(3) Relative occurrence of elements and compounds, it seems, may be learned from reference to geology. The chemistry student gazing at a periodic chart day after day has little means of knowing against which of the elements he is most likely to stub his toe. A geologist tells us[5]:

> Every chemist should have some familiarity with the subject [abundance and distribution of elements in the earth's crust], but the general experience of those whose work deals with raw materials has been that many chemists are not acquainted with the sources of the elements and compounds that they use.

Might it not be well for a chemistry student to look to the earth as well as to the periodic chart? We are told that silicates are the most frequently encountered compounds; silicates of all but a few of the metals exist in nature, and SiO_2 may constitute about 60 per cent of the earth's crust. Next in abundance are the carbonates.[6] Yet how often does proportionate time for class study of silicates or carbonates give any idea of their natural importance?

We have yet much to learn from the earth's crust. We are told[7] that:

> Most of the earth's crust is composed of elements of low atomic number. Those of even atomic number are far more abundant than those of odd atomic number.... The entire pattern of the abundance of the elements reflects laws, not yet fully understood, that govern the way in which neutrons, mesons, protons, and electrons are and can be assembled to form the elements.

(4) Economic aspects of matter seem important to consider. At an Earth Science Institute at Harvard, Kirtley Mather deplored the widespread lack of knowledge and appreciation of the earth's natural resources. It was agreed that "knowledge of the basic materials and environmental conditions that support our national prosperity and industrial economy, particularly the role of soil, water, and minerals, should be a part of every citizen's education."[8]

Assuredly, chemistry courses cannot bear the responsibility for this part of "education for citizenship." Yet there are unique opportunities in chemistry; for example, in the study of metals there may be developed some understanding of why the deposits are where they are, their relative abundance and importance, and the citizen's responsibility in wise "resource use." The greater emphasis on organic chemistry in beginning general chemistry is of necessity closely related to our deposits of coal and petroleum. Even the current popularity of uranium prospecting indicates there is some connection between chemistry and economic geology!

(5) Industrial applications indicate the dependence of chemical industry on geological factors. In the writer's home limestone region, it is the practice of our general-chemistry classes to visit a lime works: first the quarries where a geologist explains the formation of the calcium carbonate, the dolomitic, silica, and iron impurities; then the plant itself where an engineer explains the changes carried on in the kilns; finally the analytical laboratory where the chemist explains the routine testing, necessary because of variations in the limestone. Surely this going "back to the earth" is more meaningful than merely heating c. p. calcium carbonate in a crucible and writing in a manual:

$$CaCO_3 \rightarrow CaO + CO_2\uparrow$$

One wonders if Charles Martin Hall would have been inspired to find a means of electrolysis for aluminum ore if his professor at Oberlin had not "digressed" to discuss the abundant geologic distribution of aluminum, as well as the metallurgical problems related to its recovery.

(6) Analytical experience (qualitative or quantitative) in general chemistry could well include more geological materials and methods. Dr. Pauling,[9] in his denunciation of the uselessness of "traditional" qualitative analysis, suggested analysis by use of the geologist's hardness scale (Moh's scale) as one of the means of identification, and the giving of a solid substance (mineral crystal) as an unknown. "What's in this rock I found?" seems to be a better psychological approach than "What's in this solution the lab instructor concocted?" (True, it is more difficult, and requires a better chemist to find the answer!)

(7) Understanding of fundamental principles of life requires a "broad-fields" approach, not only in chemistry, but in geology and many other sciences. We agree fairly well now that chemistry should begin with atomic structure, radioactivity, and the like. Just what does a "half-life of 2.7×10^6 y." mean to a chemistry student with no concept of geologic time? "The concept of time is of prime importance in understanding geology,"[10] but it seems fundamental also in any other science—and in life itself. Where did matter originate? Is the absolute predictability of chemical change purely accidental? What significance do order and plan in the universe have in daily life? Perhaps these *are* cultural values, and the sciences alone will not supply all the interpretations. Should they be omitted from the general-chemistry courses? Should we teach only facts,

[5] FLEISCHER, *loc. cit.*

[6] SMITH, ORSINO C., "Identification and Qualitative Chemical Analysis of Minerals," D. Van Nostrand Co., Inc., New York, 1953, p. 102.

[7] FLEISCHER, *loc. cit.*, p. 448.

[8] NICHOLS, HERBERT B., "Earth science institute," *Science*, 113, 757 (1951).

[9] PAULING, L., Address presented before the Sixth Conference on the Teaching of Chemistry, Fisk University, June 15, 1955.

[10] HOLMES, CHAUNCEY D., "Geology in the liberal arts college," *Sci. Monthly*, 73, 194–7 (1951).

or shall we give the students a framework for organizing those facts into a meaningful whole? More geology in chemistry courses may help; it is at least a beginning.

Need we fear that chemistry will "suffer" as it is broadened, particularly for the nonscience major? There is a:

> ...common assumption that any emphasis on cultural value in an introductory science course tends to nullify its pre-professional effectiveness because, according to the assumption, such a course is necessarily "sugar-coated" or "watered-down." Any course *can* be "watered down" but no college course worthy of credit need be. The task of bringing into focus the human significance of scientific knowledge requires intellectual effort and teaching skill of the highest order.[11]

"Down to earth" for some good chemistry teaching!

[11] *Ibid.*

THE QUALITATIVE SEPARATION AND DETECTION OF ZINC

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MANY instructors of inorganic qualitative analysis have been confronted by a student who in some manner has completely "lost" the zinc ion from a known solution containing all of the ions commonly found in the Group III (iron, zinc group) cations of the qualitative inorganic scheme of analysis. Sometimes the known solution of the Group III cations has been prepared by the instructor; at other times it has been made up by the student himself from stock solutions kept for that purpose.

When questioned as to his procedure of analysis, the student always maintains that he has followed exactly the procedure outlined in the text for the course. The fact that many students have great difficulty with the detection of zinc in qualitative analysis seems to indicate that there might be some stages in the qualitative inorganic scheme of analysis where the zinc ion could be adsorbed on or coprecipitated with precipitates of other ions in the group. The wide applicability of radioisotopes as tracers has made it very simple to follow the zinc ion through the qualitative scheme of analysis and to determine quantitatively the amount of zinc coprecipitated with or adsorbed on precipitates of other members of the Group III cations.

The scheme of analysis chosen for these experiments closely followed that described by Engelder[2] except that no attempt was made to separate either the nickel from the cobalt or the iron from the manganese. A brief outline of the scheme is as follows: About one gram of solid NH_4Cl was added to the solution containing all of the cations commonly found in Group III of the qualitative scheme of analysis. The solution was then made slightly basic with dilute NH_4OH and then strongly ammonical by addition of an excess of 2 ml. of concentrated NH_4OH. The solution was heated nearly to boiling and H_2S was passed into the hot solution for a period of four minutes. The precipitate was centrifuged and washed. Ten ml. of 1:9 HCl was added and the precipitate was allowed to stand for a period of three minutes. The precipitate was again centrifuged and the supernatant liquid, containing all of the ions of the group except nickel and cobalt, was evaporated to a small volume. While this evaporation was proceeding, the precipitate of NiS and CoS was washed, mounted in a one-in. planchet, and dried under infrared light.

After the supernatant from the nickel and cobalt separation had been evaporated to a small volume, the solution was made strongly basic with NaOH, and one gram of solid Na_2O_2 was added. The solution was boiled to expel the excess peroxide and then centrifuged. The supernatant from this separation contained aluminum, chromium, and zinc. The precipitate containing iron and manganese was washed, mounted in a planchet, and dried in the same manner as the nickel and cobalt precipitate. The supernatant was made acid with dilute HNO_3, and solid NH_4Cl again was added. The solution was then made strongly ammonical with NH_4OH and centrifuged. The precipitate of $Al(OH)_3$ was washed, dried, and mounted as above, and the supernatant was made faintly acid with acetic acid. Sodium acetate was added and the chromium precipitated as $BaCrO_4$. The chromium precipitate was

[1] Present address: Department of Chemistry, The Citadel, Charleston, South Carolina.

[2] ENGELDER, C. J., "A Textbook of Elementary Qualitative Analysis," 3rd ed., John Wiley & Sons, Inc., New York, 1947.

Amounts of Radioactive Zn^{65} Found in the Precipitates of Various Other Ions of Group III

Concentration of all Group III ions	*Total Zn recovered, %*	*Zn^{65} found in the precipitates of*					
		Co and Ni, %	*Fe and Mn, %*	*Al, %*	*Cr, %*	*Zn, %*	*Combined wash solutions, %*
0.001 *M*	94.5	1.6	8.5	3.9	2.9	77	0.6
0.002 *M*	96.9	1.0	8.6	3.3	2.8	79.9	1.3
0.004 *M*	95.9	1.1	8.2	3.5	2.7	79.1	1.3
0.01 *M*	96.4	1.2	7.7	8.0	2.8	75.7	1.0

centrifuged, washed, dried as above, and mounted in a planchet. The supernatant was heated to boiling and H_2S was passed in for a period of four minutes to precipitate ZnS. The precipitate was centrifuged, washed, dried, and mounted as described above.

EXPERIMENTAL

Solutions containing all of the ions commonly found in Group III of the qualitative scheme of analysis were prepared. The concentration of each ion in the first solution was 0.001 *M;* in the second, 0.002 *M;* in the third, 0.004 *M;* and in the fourth, 0.01 *M*. Twenty-five lambda (0.025 ml.) of radioactive Zn^{65} was added to an aliquot of 50 ml. of solution prior to precipitation with H_2S. The radioactive Zn^{65} was chosen because its half-life of 250 days[3] eliminated the necessity for corrections to the activity due to decay during the time of the separations of the ions in the group.

For each of the concentrations as listed in the table, four separate runs were made. The combined precipitate of nickel and cobalt sulfides was measured as a single sample, as was the combined precipitate of iron and manganese. The aluminum, chromium, and zinc precipitates were each measured separately. The combined wash solution from the entire procedure was evaporated to dryness, mounted in a planchet, and measured for Zn^{65} activity.

The activity of each of the precipitates and the wash solution was measured by means of an integral gamma scintillation counter similar to the one described by Fairstein.[4] The activity found in the precipitates was compared with the activity of a standard sample prepared by mounting 25 lambda of the radioactive Zn^{65} in a planchet and drying under infrared light. The ratio of the amount of activity found in a precipitate compared to the activity of the standard sample gave the percentage of zinc in that precipitate. The results of these experiments are shown in the table.

RESULTS

As shown in the table, the amount of zinc recovered as ZnS was always greater than 75 per cent. The total amount of zinc recovered in the entire scheme of analysis ranged from 94.5 to 96.9 per cent. The greatest consistent loss of zinc occurred in the combined iron and manganese precipitates. This fact is not unexpected since both $Fe(OH)_3$ and MnO_2 are often used in radiochemical separations as "scavengers" for small amounts of unwanted contaminants.

It was rather surprising to find that changes in the concentration of the ions of Group III did not seem to affect the amounts of zinc found in the various precipitates of the other members of the Group III cations; but with the exception of the aluminum precipitate in the runs where the concentration of all the ions was 0.01 *M*. This is probably due to the increase in the amount of adsorption or occlusion of the zinc by the gelatinous $Al(OH)_3$.

It was found that the time the group precipitate was in contact with the 1:9 HCl for the separation of the nickel and cobalt sulfides from the other members of the group had a great effect on the amount of zinc found in the combined cobalt and nickel precipitate. If the group precipitate was left in contact with the 1:9 HCl for two or three minutes, as given by Engelder[2] in his procedure, the zinc sulfide was almost completely dissolved. However, if the 1:9 HCl was in contact with the group precipitate for less than one minute, large amounts of Zn^{65} activity were found in the combined cobalt and nickel precipitates.

The fact that 100 per cent of the zinc was not accounted for in this procedure can very probably be explained by the tendency of ZnS to cling to the glass vessels used in the final precipitation of zinc with hydrogen sulfide, and to the loss occasioned by the transfer of the various solutions and precipitates to a large number of beakers and centrifuge tubes throughout the procedure.

CONCLUSIONS

The results of these experiments indicate that when the procedure as outlined in Engelder[2] is followed correctly, not less than 75 per cent of the zinc will be found as ZnS in the scheme of analysis. The recovery of such an amount of zinc is certainly more than sufficient for any qualitative scheme of analysis. It would not seem worth the time and effort required to redissolve and reprecipitate the combined iron and manganese in order to recover additional small amounts of zinc.

[3] LIVINGOOD, J. J., AND G. T. SEABORG, *Phys. Rev.*, **55**, 457 (1939).

[4] FAIRSTEIN, E., *Rev. Sci. Instr.*, **22**, 76 (1951).

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IMMUNOCHEMISTRY: THE CHEMISTRY OF ANTIGENS AND ANTIBODIES[1]

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IMMUNOLOGY as a branch of biology and medicine is based on the observation that human and animal organisms which survive a bacterial infection become immune to a later infection of the same type. It was soon discovered that the blood serum of the immune organism is able to agglutinate the invading microorganisms, to dissolve them, or to cause their engulfment by the body cells, a process called phagocytosis. All these reactions were found to be quite specific; the immune serum acts only on those microorganisms whose previous invasion had been overcome. Owing to the predominant role of the blood serum in these reactions this branch of immunology is frequently designated as serology. The active factor of the blood serum which causes agglutination, bacteriolysis, or phagocytosis is called an *antibody*, and the microorganism which gives rise to the production of antibodies is called an *antigen*.

Although the action of antibodies is beneficial when they cause immunity, they also may lead to phenomena which are detrimental to the organism. Thus, if a guinea pig that had been injected with horse serum and in whose body antibodies against horse serum circulate is reinjected with horse serum several weeks or months later, serious disturbances such as respiratory asthma or shock are observed and the animal may die. The phenomena occurring after reinjection of an antigen are called anaphylactic reactions. Since the antibody formation in such cases is an unfavorable reaction, the term "immunization" is replaced by "sensitization." It must be kept in mind, however, that both immunization and sensitization are, essentially, identical phenomena based on the formation of antibodies.

ANTIGENS AND HAPTENS

In the preceding section it has been shown that antibody formation can be accomplished by two types of antigen: (*a*) particulate antigens such as microorganisms, and (*b*) soluble antigens such as those present in horse serum. Since the immunity phenomena in man were discovered first in persons who had overcome bacterial infections, immunology in its beginning dealt mainly with bacterial or cellular antigens. Later it was discovered, however, that each of the microorganisms used as an antigen contains a multiplicity of soluble antigens. Some of these are proteins, others polysaccharides or complexes formed by proteins, carbohydrates, and lipids. Hence, injection of such a microorganism may give rise to the formation of various types of antibody. Obviously, it is preferable to study the formation of antibodies under the simplest conditions—for instance, after injection of a single well-defined antigen.

The first step in this direction was made by R. Kraus (1898) who discovered that antibody formation can be induced by the injection not only of bacteria, but also of bacterial extracts. Later it was found that most proteins act as antigens if they are administered to an animal of a foreign species parenterally, *i. e.*, by intravenous, subcutaneous, intramuscular, or intraperitoneal injection. The antibodies produced in response to the injection of a foreign protein combine with this protein forming, in many instances, an insoluble precipitate. Antibodies of this type are designated as *precipitins*. Other antibodies form soluble antigen-antibody complexes; they have been called *reagins*. If the antigen is a toxic substance like diphtheria toxin or the toxin of snake venom, the antibody is called an *antitoxin*.

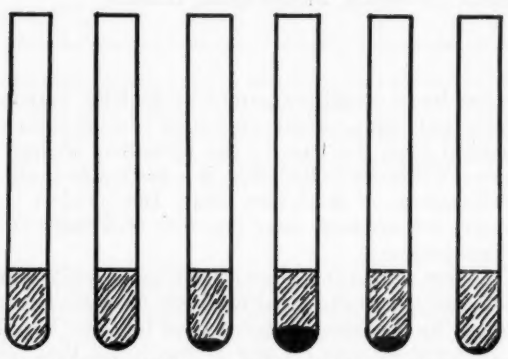
Although most vertebrates form antibodies, the antibody level of the blood serum may be very low. The highest antibody levels are found in horses and rabbits. Therefore, these animals are preferentially used for the production of immune sera. The antigen must be injected parenterally; if antigens are given orally they are destroyed by the enzymes of the gastrointestinal tract or are excreted without being absorbed.

The test used for the detection of precipitating antibodies is called the *precipitin test*. Its result is shown in the figure, where each of the small precipitin tubes contains 0.1 ml. of the investigated immune serum and 1.0 ml. of the antigen solution. The concentration of the antigen decreases in a geometrical series from high to low concentration. As shown by the figure, the largest amount of precipitate is formed at an intermediary concentration. Evidently the precipitate is soluble in an excess of antigen. It is insoluble, in general, in an excess of antibody or of the antibody-containing immune serum. The precipitin test can be used to determine the animal species from which a protein originates. It also is used to detect the fraudulent addition of horse meat to meat preserves. The only reagent needed in such an examination is the serum of a rabbit which has been sensitized by injection of horse proteins. Such a serum gives precipitates when mixed

[1] The experimental work described in this paper was supported by research grants from the U. S. Public Health Service and the American Cancer Society, and by contracts of Indiana University with the U. S. Atomic Energy Commission and the U. S. Office of Naval Research.

with an extract of horse meat, but does not precipitate proteins of any other animal species.

For a long time it was believed that the protein molecule as an entity acts as an antigen and that the specificity of the antibody is directed against the whole protein molecule. However, in 1912 Obermayer and Pick



Each of the small precipitin tubes contains 0.1 ml. of the immune serum and 1.0 ml. of the antigen solution. The per cent concentration of the antigen (*from left to right*) is: 0.3, 0.1, 0.03, 0.01, 0.003, and 0.001.

demonstrated that the serological specificity of proteins is deeply altered by iodination. In this procedure iodine atoms substitute the 3 and 5 positions of the phenol ring in the tyrosine residues of the protein. If a rabbit is injected with iodinated horse-serum protein, it forms antibodies which precipitate not only the iodinated horse-serum protein, but also iodinated human- or chicken-serum proteins, iodinated ovalbumin from hen's eggs, and other iodinated proteins; however, they do not precipitate the native horse-serum proteins. Evidently the antibodies combine with the 3,5-diiodophenol group only. These experiments demonstrate clearly that the antibodies react with definite chemical groups in the antigen molecules and that the serological specificity is, essentially, chemical specificity. Shortly thereafter, in 1914, this was proved beyond any doubt by the brilliant work of Karl Landsteiner who is considered the founder of immunochemistry (*1*).

Landsteiner coupled proteins with diazotized aromatic amines or amino acids. In this reaction the tyrosine and histidine residues of the proteins are substituted by various azoaryl groups. The reaction proceeds very smoothly under mild conditions (pH 8–10 at 0°) so that the protein does not undergo denaturation. The azoproteins formed by this reaction are red or brown substances, soluble at pH 7, precipitable by acidification. If they are injected into rabbits, the animals produce antibodies which react quite specifically with the aromatic residues. Thus, coupling of a protein with diazotized sulfanilic acid gives rise to the formation of antibodies combining with the *p*-azophenyl sulfonate group. The reaction is highly specific. Antibodies to *p*-azophenylsulfonate groups do not combine with proteins carrying *o*- or *m*-azophenylsulfonate groups, or with *p*-azophenylarsenate or *p*-azobenzoate groups. Antibodies formed in response to azoproteins containing *m*-azophenylsulfonate groups combine with *m*-azophenylsulfonate, but not with *o*- or *p*-azophenylsulfonate groups. Landsteiner was able to prepare azoproteins containing *d*- and *l*- isomers or *cis*- and *trans*- isomers, and to show that antibodies can differentiate between *d*- and *l*- compounds and between *cis*- and *trans*- compounds. There is no doubt, therefore, that *the specificity of each antibody is directed toward a definite chemical group of the antigen molecule* and not toward the antigen molecule as an entity. We call the serologically active groups of antigens *determinant groups*.

Landsteiner, in his fundamental investigations, observed that most of the determinant groups of azoproteins were acidic groups. Later we found that strongly basic groups such as *m*-azophenyl-trimethylammonium groups likewise were serologically determinant. We conclude, therefore, that polarity is one of the prerequisites for the specific determinant groups of the antigen (*2*). Another prerequisite is, apparently, a certain rigidity of the determinant groups. This may be the reason why the rigid structures of the aromatic amines are so strongly determinant. If diazotized, aminophenyl fatty acids are attached to proteins, the fatty-acid residues of different chain lengths cannot be differentiated from each other by serological methods. This is evidently due to the lack of rigidity in their paraffin chains.

In order to induce the formation of antibodies, the determinant groups must be attached to a protein molecule. It presumably acts as a carrier, transporting the determinant group to the sites of antibody formation. Although small, protein-free molecules which contain determinant groups are not able to induce the formation of antibodies, antibodies formed after the injection of an antigen containing a determinant group will combine with the protein-free determinant group. Thus, antibodies produced by the injection of an azoprotein containing *p*-azophenylsulfonate groups, —N=N—C_6H_4—SO_3H, combine readily with *p*-azophenylsulfonate derivatives of tyrosine, histidine, or phenol. In the immunochemical terminology, molecules which combine specifically with the antibody but are not able to induce antibody formation are called *haptens*. Most of the hapten complexes are water-soluble. The antibody moiety of these complexes has a high molecular weight; therefore, the formation of hapten-antibody complexes can be demonstrated by equilibrium dialysis.

Since hapten, as well as antigen, combines with the homologous antibody, the formation of insoluble antigen-antibody precipitates can be prevented by large amounts of hapten. This method has been used to determine the affinity between the determinant group of the antigen and the combining group of the antibody, and to calculate the closeness of the "fit" between the two combining groups (*3*).

THE NATURE OF ANTIBODIES

Antibodies are found in the globulin fraction of the immune sera. They are salted out by half saturation with ammonium sulfate, and they migrate on electrophoresis with the serum globulins, chiefly with the γ-globulin fraction. The amino acid composition, the N-terminal amino acids, the molecular weight, and other physical-chemical properties of the antibodies are identical with or very similar to those of the γ-globulins of the blood serum (*4*, *5*). Obviously, there must be some difference between antibodies and normal serum γ-globulins since the antigen which induces the formation of an antibody combines quite specifically with the homologous antibody, but not with other antibodies nor with normal serum globulin.

The first theory on the nature and formation of antibodies was advanced in 1891 by Paul Ehrlich, the founder of immunology, whose centenary was celebrated throughout the world in 1954. According to Ehrlich the normal organism contains small amounts of all possible types of antibody. After injection the antigen is trapped by the corresponding preformed antibody, called by Ehrlich *receptor*. Receptors of this class are then regenerated and pass into the blood serum where they act as antibodies. The relation between antigen and antibody was considered by Ehrlich to be one of "complementariness in shape" between the invading bacterium and the cells which act as receptors.

Ehrlich's views were accepted over a long period of time. Although his idea of mutual complementariness, when applied to molecular dimensions, is still valid, the idea of preformed receptors had to be modified after Landsteiner's discovery of the antigenicity of azoproteins. It was hard to believe that the organism should possess preformed antibodies against azophenylsulfonate or azophenylarsenate in *o*-, *m*-, and *p*-position—in other words, antibodies against artificial products of the chemical laboratory.

In 1930, Breinl and the author (*6*) investigated the precipitin reaction by quantitative methods and found that the composition of the precipitate varied within very narrow limits only. Using hemoglobin as a colored antigen, we found that the weight ratio of serum globulin to hemoglobin was approximately five at high hemoglobin concentrations, and about ten when an excess of the immune serum was used. The nonhemoglobin portion of the precipitates had all the properties of serum globulins. We concluded, therefore, that the precipitated serum globulins were not contaminants of antibody molecules of unknown nature, but that the antibody molecules themselves were globulins. It was well known at that time that antibodies do not appear in the blood immediately after injection of the antigen, but that there is a lag period of a few days before the antibody titer of the blood serum rises noticeably. We therefore advanced the view that the injected antigen interferes with the process of globulin synthesis so that globulin molecules complementarily adjusted to the shape of the determinant groups of the antigen are formed. These are the antibodies. Similar theories were advanced independently by Mudd (*7*) and Alexander (*8*).

To test this theory we investigated the distribution in the rabbit organism of an azoprotein containing *p*-azophenylarsenic acid groups. We found that most of the injected antigen was deposited in the liver, spleen, and bone marrow, *i. e.*, in those organs which are considered to be the sites of serum protein formation. In recent years we repeated these experiments with antigens labeled by traces of radioactive isotopes. Such antigens can be produced easily by iodinating proteins with I^{131} or by coupling proteins with diazotized S^{35}-sulfanilic or C^{14}-anthranilic acid (*9*). We found that heavily substituted iodo- or azoproteins, containing from 10 to 20 moles of the substituent per 10^5 g. protein, are eliminated from the blood serum from one to two hours after the intravenous injection and are deposited in the organs of the reticulo-endothelial system (liver, spleen, bone marrow, lung), where the protein-bound radioactivity persists for many months, possibly for years. Four weeks after the injection of an azoprotein containing *p*-azophenylsulfonate groups, we found most of the protein-bound S^{35} of the liver in arylsulfonate groups; only three per cent of the protein-bound S^{35} was present as cystine or methionine. It cannot yet be decided whether the arylsulfonate groups remain bound to their original protein carrier or whether they are transferred by transpeptidation to the tissue proteins. Since the serological specificity of such heavily substituted azoproteins resides in their azophenylsulfonate groups, and not in the protein carrier, this problem is not of primary importance.

The situation is different when I^{131} or S^{35} substituents are used in small amounts only as trace labels for more or less unchanged proteins. If labeled antigens of this type are injected, most of the antibodies formed are directed against the protein component and not against the radioactive label. Thus, injection of beef serum globulin, labeled by traces of diazotized S^{35}-sulfanilic acid, gives rise to the formation of antibodies which precipitate native or trace-labeled beef-serum globulin, but not the heavily substituted azo beef-serum globulin. The trace-labeled, beef-serum globulin circulates in the blood of rabbits for from four to six days without noticeable storage in organs. After the onset of antibody formation, antigen-antibody complexes are formed and deposited in the reticulo-endothelial organs (*10*).

The high sensitivity of the radioactive methods allows us to investigate the distribution of antigens within the tissues and cells. In such investigations the organs of the injected animals are homogenized and the homogenate is fractionated by differential centrifugation. At low speeds the nuclei are centrifuged off, at higher speed mitochondria and other cytoplasmic

granules, and at the highest speed submicroscopical particles called microsomes. They can be made visible by electron microscopy. The proteins of these three fractions and those of the supernatant cell fluid were precipitated by trichloroacetic acid and counted. In all our experiments we found that the deposited radioactivity was concentrated in the proteins of the cytoplasmic granules (mitochondrial and microsomal fraction), whereas the radioactivity of the proteins in the nuclear and supernatant fractions was low.

To preclude fallacies by the transfer of the antigen from one fraction to the other during homogenization procedure, we also analyzed histological sections of the organs by autoradiography. In this method thin sections of the tissue are coated by a photographic emulsion and kept protected from light over several weeks or months, depending on the half-life of the isotope used. The radioactive material in the tissue sensitizes the silver halide of the photographic layer which, after developing and processing, is converted to black silver granules. The tissue is stained before or after the photographic procedure and the position of the silver granules is observed by microscopy. By means of this method the results of the homogenization procedure were confirmed. The concentration of the antigen was found to be higher in the cytoplasm than in the nuclei. Autoradiography also allowed us to localize the antigen in small organs such as the lymph nodes. Most of the radioactivity was localized in the macrophages; these are large phagocytic cells which engulf not only antigen molecules but also larger antigen particles such as bacteria.

In all these experiments the antigen molecules were proteins labeled by an external label like iodine or azophenylacyl groups, externally attached to the protein carrier. Obviously, these experiments do not reveal anything about the metabolic fate of the protein portion of the antigen. Recently we have begun to work with radioactive proteins prepared by injecting radioactive S^{35}-amino acids into guinea pigs, chickens, or other animals. If these internally labeled proteins are labeled externally by iodine or by C^{14}-azo compounds, doubly labeled antigens are obtained. When such doubly labeled antigens were injected into rabbits or rats, it was found that the internal label persisted in the liver and lymph nodes for long periods of time, indeed, much longer than the external label (*11*). We consider this to be a strong argument in favor of our theory on the formation of antibodies. If antibodies, as postulated by this theory, are formed as negative prints of the antigen molecule, then the presence of the antigen is necessary for antibody formation, and antibody formation cannot continue after the elimination of all of the antigen from the organism.

Many immunologists are reluctant to accept this conclusion because immunity to some of the bacterial or viral infections lasts many decades, in some cases the whole life. It is difficult to imagine that the antigenic proteins or polysaccharides of invading bacilli should persist in the organism for such long periods of time. One would reasonably expect that the proteins or polysaccharides are digested by intracellular enzymes within a few days or weeks. On the basis of these arguments, Burnet and Fenner (*12*) proposed a theory of antibody formation according to which the antigen causes the formation of specific enzymes which in turn produce antibodies and continue to produce antibodies after the elimination of the antigen.

Although this theory is very attractive to immunologists and pathologists, who do not deal with antigen molecules but with bacteria and viruses, it does not answer the question of the mechanism of antibody formation but shifts the problem to that of the formation of hypothetical enzymes of high specificity. Burnet compares these enzymes with the so-called "adaptive enzymes" which can be produced by raising yeast or other microorganisms on culture media containing an unusual nutrient. It is well known, however, that adaptive enzymes are formed only as long as the uncommon nutrient is present. After its removal, the formation of the adaptive enzymes is discontinued. Another objection raised against Burnet's theory is based on the formation of antibodies against antigens containing artificial determinant groups. It is difficult to believe that the organism should be able to form enzymes adapted to artificial chemical substances such as azophenylarsenate derivatives.

Burnet's theory is based mainly on the belief that antigens cannot persist in the organism without being degraded and metabolized. However, in the preceding paragraphs it has been demonstrated that protein antigens persist in the organism for an astonishingly long time. The sensitive methods of radiochemistry fail when the average antigen concentration of a tissue drops to less than a few hundred antigen molecules per cell, an amount which is still present one year after the injection of azoproteins to a rabbit. It must not be forgotten, however, that only a few of the cells are antibody producers and that an average antigen content of 100 antigen molecules per cell may be equivalent to 1000 or 10,000 antigen molecules per antibody-forming cell.

While many of the bacterial antigens and toxins are proteins, the antigens of the capsule of pneumococci and other bacteria are polysaccharides built of various hexoses, hexuronic acids, and aminohexoses. Felton (*13*) recently has shown that these polysaccharides, which are highly antigenic for mice, persist in the mouse organism for many months after injection without being degraded. It is difficult to explain this long persistence of protein and polysaccharide antigens. Most probably they are first engulfed by cells of the reticulo-endothelial system, and then protected against the action of intracellular enzymes by combination with other intracellular components such as lipids, nucleic acids, or mucopolysaccharides. Indeed, they seem to persist in the cells just as do particles of India ink or the pigments which are used for tatooing, and

remain in the tissues over many years. In view of our findings we believe that formation of antibodies over many years is due simply to the persistence of antigens.

What is then the mechanism of antibody formation? How is the complementariness of their molecules accomplished? We cannot expect a satisfactory answer to these questions as long as we do not know more about the mechanism of the biosynthesis of proteins. The antibody molecule, like that of other globulins, consists of a long peptide chain which by folding assumes globular shape. It is reasonable to assume that the biosynthesis of such a molecule takes place in two steps: (*a*) formation of the long peptide chain, and (*b*) folding of this chain (*14*). As mentioned before, the amino acid composition of the antibodies is hardly different from that of the normal γ-globulins of the blood serum. Porter (*15*) and E. L. Smith (*5*) have found that the sequence of the five N-terminal amino acids of rabbit antibodies is the same as that of normal rabbit-serum γ-globulin. Although this does not entitle us to extrapolate to a long peptide chain formed by more than 1000 amino acids, it is quite possible that the peptide chains of the antibody molecules are identical with those of normal γ-globulins and that antibody molecules differ from the normal γ-globulins only by the mode of folding of the peptide chain (*16*), *i. e.*, by their "constellation" (W. Kuhn) or "conformation" (Eyring).

We assume that the determinant group of the antigen acts as a template for the specific combining group of the antibody molecule. Complementariness, according to this picture, is accomplished by the folding of the peptide chains in such a manner that the combining group of the antibody forms a negative print of the determinant hapten group of the antigen. Antigens, according to this view, would not interfere with the first phase of protein synthesis, the formation of the peptide chains, but with the second phase, the folding of the peptide chains. Since we find most of the antigen in the cytoplasmic granules of spleen, lymph nodes, and liver, it may be that antibody formation takes place in the cytoplasm and not in the nucleus. This assumption is supported by the fact that acquired immunity is not a hereditary characteristic and is never transmitted from parents to the next generation.

COMBINATION OF ANTIGEN WITH ANTIBODY

Although we know a number of different immunological phenomena such as precipitation, agglutination, phagocytosis, and hemolysis, they all share one common phase; namely, the combination of antigen with antibody molecules. This combination is brought about by the mutual complementariness of the combining groups of antigen and antibody. The adjustment in shape allows the molecules to come so close to each other that *short-range* forces become very powerful and attraction by van der Waals forces, dipole induction, and London forces results. Inhibition experiments with haptens indicate that the fit between antigen and antibody is very close and that deviations of from one to two Å. have a significant influence on the mutual affinity of antigen and antibody (*3*).

The precipitin test can be carried out as a *quantitative* test by measuring the amount of precipitate and analyzing it for its content of antigen and antibody. Heidelberger and his co-workers (*17*) determine the nitrogen content of the precipitate by Kjeldahl analysis, whereas gravimetric analysis is used in the author's laboratory (*18*). Very small amounts of precipitate can be dissolved in alkali; the protein content of the solution can then be measured by determining the optical density of the solution in ultraviolet light. If the antigen is a colored protein like hemoglobin or hemocyanin, it can be determined in the precipitate by colorimetric analysis; the antibody content of the precipitate is then calculated by subtracting the weight of the antigen from the total weight of the precipitate. However if the antigen is a colorless protein it is very difficult to determine it in the presence of antibody protein. This difficulty can be overcome by labeling antigen or antibody by traces of radioactive isotopes and measuring the intensity of the radiation.

The molar ratio of antibody to antigen in the precipitate always has been found to be larger than 1.0. Hence, it is assumed that the antigen molecule is "multivalent," *i. e.*, that it has more than one combining determinant group. It is easy to prepare azoproteins with from 10 to 50 determinant azophenylacyl groups per molecule. The antibody to antigen ratio in such precipitates is very high, varying from five to about 30 antibody molecules per antigen molecule. Antigens with one or two determinant groups per molecule do not seem to form insoluble precipitates.

It is not yet clear whether the antibody molecules have one or more combining groups. Some of the antibody molecules do not precipitate the homologous antigen, but form soluble antigen-antibody complexes. They are considered by some immunochemists to be poorly adapted antibodies, by others to be "univalent" antibodies, *i. e.*, antibodies containing only one combining group. In view of these results it is not yet clear whether the insoluble antigen-antibody complex, which forms the precipitate, consists of an alternate antigen-antibody lattice or rather of numerous aggregates, each consisting of a multivalent antigen molecule as nucleus to which numerous antibody molecules are bound.

The affinity between antigen and antibody can be measured by dissociating antigen-antibody complexes and measuring the dissociation constants at different temperatures. Experiments of this type show that the free-energy change, ΔF, for the combination of loosely bound antibodies in the precipitate is approximately −7 to −10 kg.-cal. per mole of antibody, but that it is much higher for the firmly bound antibodies which cannot be split off from the precipitate. The heat of combination is very low, varying from one to

four kg.-cal./mole; the entropy of combination is positive, probably owing to the release of water molecules from the combining groups (*19*).

Most antigens have not only a large number of determinant groups, but also a variety of such groups. This also is valid for proteins substituted by a small number of artificial determinant groups. Thus, partially iodinated proteins in addition to their iodinated groups also contain the species specific groups of their protein carrier. Accordingly, injection of iodinated beef-serum globulin to a rabbit gives rise to the formation of at least three types of antibody: (*a*) antibodies combining with the iodinated residues (*anti-I*), (*b*) antibodies combining with the species-specific groups of beef-serum globulin (*anti-BG*), and (*c*) antibodies combining with a complex formed by both types of determinant group (*anti-IBG*). The three types of antibody can be separated from each other and determined quantitatively by means of suitable test antigens. Thus, *anti-I* is precipitated by iodinated ovalbumin, and *anti-BG* by native beef-serum globulin; all three antibodies are precipitated by iodinated beef-serum globulin. The table shows the result of the serial addition of various test antigens to three ml. of an immune serum against iodinated beef-serum globulin. According to the table the total amount of antibody is 9.8± 0.5 mg.; it does not depend on the sequence in which the test antigens are added. Quite generally, a variety of antibodies is formed in response to a single antigen.

Fractional Precipitation of Antibodies Formed in Response to the Injection of Iodinated Beef-serum Globulin to a Rabbit[a]

Experiment number	*Added*	*P.*	*Ag.*	*Ab.*
1	I-BG	9.62	0.96	8.66
	I-BG	1.73	0.23	1.50
	BG	0	0	0
			Total	10.16
2	I-Ov	4.52	0.92	3.60
	I-Ov	trace	trace	trace
	I-BG	5.78	0.66	5.12
	I-BG	1.75	0.40	1.35
	I-GB	trace	trace	trace
			Total	10.07
3	I-Ov	4.37	0.41	3.96
	I-Ov	trace	trace	trace
	BG	0.64	0.16	0.48
	BG	trace	trace	trace
	I-BG	4.68	0.86	3.82
	I-BG	1.36	0.30	1.06
	I-BG	trace	trace	trace
			Total	9.32
4	BG	1.17	0.29	0.88
	I-Ov	4.53	0.65	3.88
	I-Ov	trace	trace	trace
	I-BG	4.31	0.75	3.56
	I-BG	1.81	0.38	1.43
	I-BG	0	0	0
			Total	9.75

[a] Three ml. of the immune serum was precipitated by the serial addition of various test antigens, each of them added in doses of 1.2 mg. The precipitate formed after each addition was centrifuged off, washed, and analyzed for its antigen content. The figures in the table indicate mg. of precipitate (P.), antigen (Ag.), and calculated mg. of antibody (Ab.). The following abbreviations for added test antigen are used: I-OV = iodinated ovalbumin; BG = beef-serum globulin; I-BG = iodinated beef-serum globulin.

The precipitin test has been discussed so thoroughly because it is the simplest and the best investigated of all immunological reactions. Agglutination, lysis, and phagocytosis are much more complicated since cellular structures are involved in these phenomena. We speak of *agglutination* when cellular or bacterial antigens clump together after the addition of antibodies. Most of the normal cellular or bacterial surfaces are negatively charged by the presence of acidic groups of lipids, phosphoric acid residues, or acidic polysaccharides. These charges cause mutual repulsion and prevent agglutination of the cells. If the cellular surface is coated by antibody molecules, the intracellular repulsion is abolished and the cells agglutinate.

By their combination with antibody the cells also become susceptible to phagocytosis and to lysis. For lytic reactions another factor present in the native blood serum is required; it has been called *complement*. It is destroyed by keeping the immune serum for 30 to 50 minutes at 56°, whereas antibodies are not affected by this treatment. Complement is a protein complex consisting of at least four factors, designated by the symbols *C'*1, *C'*2, *C'*3, and *C'*4. None of these has been isolated in pure form. Guinea pig serum is particularly rich in complement and is frequently used in reactions involving hemolysis, for instance in the serodiagnosis of syphilis.

Agglutination, phagocytosis, hemolysis, bacteriolysis, and other serological reactions are brought about by a common principle, by the mutual complementariness of antigen and antibody molecules, and by the resulting operation of intermolecular short-range forces. It may seem astonishing, at a first thought, that dramatic phenomena such as death by anaphylactic shock can be caused by the more or less loose combination of two or more macromolecules. It must be realized, however, that the same short-range forces, the same complementariness, are responsible for the highly specific relation between enzymes and substrates, and that metabolic reactions, *i. e.*, cleavage or formation of covalent bonds, are initiated by the formation of enzyme-substrate complexes. Structural specificity and intermolecular forces also play a decisive role in the action of hormones on their target organs. All this demonstrates the paramount importance of molecular shape and of intermolecular forces in biochemical reactions.

SUMMARY

(1) Antigens are substances which interfere with the formation of proteins in the living organism in such a

fashion that proteins complementarily adapted to the determinant portion of the antigen molecule are formed. These new types of protein are the antibodies.

(2) Antibodies differ from normal serum globulins by the specific conformation of their peptide chains. Owing to their structural and spatial adaptation to the determinant portion of the antigen, the antibody molecules combine with antigen molecules and cause thereby precipitation, neutralization of toxins, agglutination, lysis, phagocytosis, or other immunological phenomena.

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THE OPERATION OF McLEOD GAGES AND TÖPLER PUMPS

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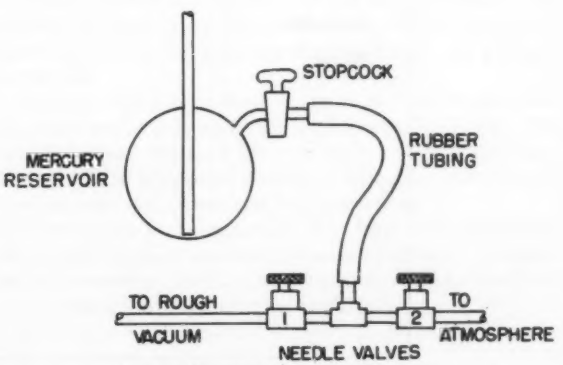
Failure to control properly the mercury level in a McLeod gage or Töpler pump can have rather unpleasant consequences for the vacuum technician. A sudden surge of mercury can result in either breakage of the system or transfer of mercury to parts of the system where its presence is undesirable. The use of float-type check valves will prevent transfer of mercury to other parts of the system, but these valves are generally subject to sticking and make the system even more susceptible to breakage as a result of mercury surges. In the case of the McLeod gage it is advantageous to mount the gage proper at a sufficient height above its mercury reservoir so that, with the reservoir open, atmospheric pressure will maintain the mercury level slightly below the gage cutoff. In order to make a pressure measurement, the mercury level is raised by application of pressure to the mercury reservoir. The author has found that this pressure can be conveniently applied and controlled by means of a rubber bulb with needle-valve control[1] such as is used on a physician's blood-pressure manometer.

Frequently, because of space limitations or large masses of mercury involved, it is necessary to mount the gage or pump immediately above its mercury reservoir. In this case the safety factor of height is lost and it is necessary to provide a means of regulating the mercury reservoir pressure rather precisely in order to prevent mercury surges. This can be accomplished by use of two needle valves as shown in the figure. With Valve 1 opened slightly, the mercury level can be regulated easily by adjustment of Valve 2. Valve 1 functions essentially as a means of controlling the sensitivity of Valve 2, giving a flexibility not possible with the fixed-capillary, two-way stopcock combination usually used. The stopcock is closed when the system is not in use since normal leakage of the needle valves will allow the mercury to rise if the source of rough vacuum fails.



Control Manifold for Mercury Reservoir

[1] "Air-Flo" control and bulb, manufactured by W. A. Baum, Inc., New York, and available from medical supply houses.

A CLASSIFICATION AND FILING SYSTEM FOR SCIENTIFIC REPRINTS AND REFERENCES

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THE care and classification of a collection of reprints present difficulties that are shared in common by all investigators. Disciplines that were considered to be clearly delimited are undergoing such changes that precedent, including standard systems of classification, *e. g.*, that of the Library of Congress, cannot be relied upon to cope with some of the radically changing orientations. The novice who seeks advice from his more experienced colleagues usually finds one or the other of the following means of collection in operation: (1) Distantly related reprints are filed under arbitrary topical headings that are subject to the whims of the investigator; or (2) reprints are shoved "temporarily" into a large unlighted closet until the investigator, who has the best intentions, but no time, "can do something about them."

Confronted with the problem of achieving and maintaining order in a collection of reprints that are pertinent to biochemistry, with emphasis on hormones and immunology, the authors have devised the system described in this report. The principles and method appear to be applicable to any body of scientific literature.

Consideration of the material that was on hand and that which was likely to be added served as the groundwork for a topical outline prepared on the basis of the primary dichotomy that Selye[1] has used so successfully. Accordingly, the literature was divided into two types; *A*. STATIC, and *B*. DYNAMIC. The primary categories were then subdivided into further breakdowns as shown in the example below.

A. STATIC DATA
- 0 Methods
  - .1 analytical
  - .2 assays
  - .3 functional
  - .4 statistical
  - .5 technical
- 1 Carbohydrates
  - .1 monosaccharides
  - .2 disaccharides
  - .3 phosphosaccharides
  - .4 polysaccharides
- 2 Proteins
  - .1 amino acids (gen.) individual amino acids listed alphabetically by initial letter
  - .2 lipoproteins
  - .3 peptides and polypeptides

Etc.

B. DYNAMIC DATA
- 1 Adsorption
- 2 Digestion
- 3 Metabolism
  - .1 Carbohydrates
    - 1 monosaccharides
    - 2 disaccharides
    - 3 phosphosaccharides
    - 4 polysaccharides
  - .2 Proteins
    - 1 amino acids (gen.) individual amino acids listed alphabetically by initial letter
    - 2 lipoproteins
    - 3 peptides and polypeptides

Etc.

Suggestions for subtopics were obtained by reading

[1] SELYE, H., "Encyclopedia of Endocrinology," A. W. T. Franks Publishing Company, Montreal, 1943.

Logane, K. A., Rens, W. J. B.
#Arch. Biol. Chem., 174,97,1946

The Assay and Distribution of a New Water Soluble Co-factor for Trypsin in Soybean Meal. Trypsin Series I.

A0.2,A6.1

Notes

A8
Log.
Ass.
Try.
I

→ Secondary designations referring to author, title, and subtitle

Primary Card

A8 Log. Ass. Try. I

Logane, K. A., Rens, W. J. B.
#Arch. Biol. Chem., 174,97,1946

The Assay and Distribution of a New Water Soluble Co-factor for Trypsin in Soybean Meal. Trypsin Series I.

Notes

A0.2 Log. Ass. Try. I

Secondary Card

the tables of contents of textbooks in biochemistry. A conventional plan was chosen for the order of listing main headings, *e. g.*, carbohydrates, proteins, etc. This type of listing seems to come readily to mind when a breakdown of main subject is attempted. In addition, wherever possible, alphabetical order was also maintained. When such a subdivision as *Metabolism* was further subdivided, every effort was made to preserve the original numbering system (see example given above). These devices reduce the amount of memorization that is necessary for efficient use of the file. It is true that the alphabetical listing will be disrupted as new substances are discovered and described, but these irregularities will not be overwhelming.

Each reprint included in the file is represented by one primary classification card and may have one or several secondary cards. The primary classification is determined by asking: "What material in this paper is of most importance to me?" For example, the paper entitled "The assay and distribution of a new water soluble co-factor for trypsin in soybean meal" by K. A. Logane and W. J. B. Rens, Arch. Biol. Chem., **174,** 97 (1946), might be processed as follows: Because it describes the distribution of coenzymes, it is classified first as *A*, static data, and then as 8, the designation for coenzymes; hence it is *A*8.

The secondary classification might be done thus: Since a method of assay is also described which may be of use at some future date, a secondary card can be prepared for category *A* 0.2, the section that is devoted to methods of assay. The secondary card also bears the primary classification number which is an expression of the location of the reprint in the file. Another secondary classification might be under trypsin, indicating that evidence for a cofactor exists.

The organizational arrangement that is given in the figures for the primary and secondary cards has been found to be both convenient and satisfactory.

The primary classification number must appear on each of the secondary cards so that the reprint may be located in the file when only the secondary card is consulted.

The upper left-hand corner of the reprint should bear the primary classification number and other designations exactly as they appear on the right-hand side of the primary card.

The dimensions of the card will vary with individual preference. The authors found it advantageous to use 4- × 6-in. cards, which are large enough to permit notation. These are filed according to the number on the right side in the order established by the original outline.

The # symbol is used to indicate that a copy of the reprint is present in the collection. Such a key may save hours of searching for a reprint that is not present in the file.

It was found expedient to save a desk drawer for reprints and cards that are withdrawn from the file, and to replace them all when there is a sizable accumulation. It is suggested, however, that the cards should not be removed unless absolutely necessary.

The criteria and suggestions that have been described have been applied successfully to a collection of papers in biochemistry, and a complete copy of the classification outline is available upon request.

✦ ✦ ✦

PREMEDICAL REQUIREMENTS AND MEDICAL COLLEGE BIOCHEMISTRY SCORES

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All students entering a given medical college have a group of premedical requirements in common. Certain courses in chemistry, physics, biology, and mathematics, as well as the Medical College Admission Test (MCAT), make up an important part of these common requirements. Biochemistry is an important basic course that is taken in the first year of medical school. In this study correlation coefficients were determined between the medical college biochemistry scores of one class of 69 students at the University of Arkansas School of Medicine, and their undergraduate grade-point averages (GPA) in (1) mathematics, (2) biology, (3) physics, (4) chemistry (all courses), (5) organic chemistry only, (6) all required science courses, and (7) all undergraduate courses. Table 1 gives these correlation coefficients.

TABLE 1
Correlation Coefficients of Medical College Biochemistry Scores with Each of the Following Undergraduate GPA's

Course	*r*
Mathematics	.355
Biology	.378
Physics	.299
Chemistry (all courses)	.333
Organic chemistry only	.243
Required science courses	.293
All undergraduate courses	.393

Correlation coefficients were also determined between the medical college biochemistry scores and the scores on the individual parts of the Medical College Admission Test: (1) Modern Society, (2) Science, (3) Verbal Ability, and (4) Quantitative Ability. Table 2 gives these values.

Two multiple correlations between the medical college biochemistry scores and predictor variables were determined. In one the predictors were the over-all undergraduate GPA and the score on the Science part of the MCAT; in the other, the predictors were the over-all undergraduate GPA and the score on the Quantitative Ability part of the MCAT. Table 3 gives these values.

Although almost all of the 69 students had their premedical work in Arkansas, a number of different colleges were represented. Since grades vary from one college to another, as well as from one teacher to another, this might help to account for the fact that the correlation coefficients with the undergraduate work were not higher. When the very close relationship between organic chemistry and biochemistry is considered, it might be surprising that this correlation coefficient was so low (.243). The fact that the organic chemistry was taken at several different colleges, in addition to the fact that the grade represents only one course of six or eight semester hours might help to explain this. It should be noted that the GPA of all of the undergraduate courses gave the highest correlation coefficient (.393).

The correlation coefficient with the score on the Modern Society part of the MCAT is conspicuously lower than the others (.041), and indicates that, with this group, there was very little relationship between that score and the score on biochemistry.

The multiple correlations shown in Table 3 are higher than the correlations in Tables 1 and 2, and indicate a stronger relationship than any of the individual correlations.

ACKNOWLEDGMENT

The authors wish to thank Dr. Joseph V. West, Professor of Psychology, Hendrix College, Conway, Arkansas, for his help and advice on the statistical work, and they wish to thank Dr. H. C. Nicholson, former Dean, University of Arkansas School of Medicine for permission to use the records there.

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TABLE 2
Correlation Coefficients of Medical College Biochemistry Scores With Scores on Each of the Following Parts of the MCAT

MCAT part	*r*
Modern society	.041
Science	.355
Verbal ability	.334
Quantitative ability	.379

TABLE 3
Multiple Correlations

	r
Biochemistry score with overall GPA-Science score MCAT	.481
Biochemistry score with overall GPA-Quantitative score MCAT	.485

* * *

DYES AND DYEING IN ANCIENT MESOPOTAMIA

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SUMER, the land of the oldest known civilization of Mesopotamia, was located in the lower reaches of the Tigris and Euphrates rivers where they approached and flowed into the Persian Gulf. Ancient Sumer was a great industrial and commercial center; its most thriving industry was the bleaching, dyeing, and weaving of wool. Of the clay tablets unearthed at Nippur, one of Sumer's largest cities, about one-sixth are concerned with records of wool and clothing (*1*). The arts of bleaching, spinning, fulling, dyeing, and weaving were fully developed by the Mesopotamians before the end of the fourth millenium B.C.

Wool, cotton, and linen were familiar to the people of Mesopotamia. Fine linen specimens were found at Susa, a large city of Elam (*2*). Linen and cotton occur from time to time in economic tablets. However, by far the favorite material for clothing was wool.

Many tablets contain lists of wool and garments, including more than 100 technical terms relating to them (*3*). Unfortunately, the technical terms used to differentiate wool from woolen garments are still obscure. The various woolens were classified both according to the garments for which intended and according to the quality, which ranged through four grades. The wool is variously described as "wool rolled on wood" (*4*), "wool rolled into balls" (*5*), "combed wool," "spun wool," and "carded wool" (*6*). An ancient contract contains the penalty for its violation: "A man shall eat one mana of carded wool. . . ." Fleece of third quality is also described (*7*), as is "cloth in the roll" (Sumerian *ŠUTUR*, Akkadian *šuturu*) (*8*).

The business stock of a merchant of Ur, as listed in a tablet, included various types and qualities of cloth wool, loose wool, black wool, dead wool, knife-torn wool, tar-soiled wool, hand-plucked wool, goat's hair, and spools of *qu* thread (*9*).

In a tablet of the second millenium B.C. found at Alalakh, detailing the annual sustenance rations, the sources of wool are indirectly referred to: "ten minas of plucked wool and ten minas of sheared wool." The former is sheep's wool and the latter goat's (*10*).

Weaving as a large operation was carried out in the weaver's house (*é-uš-bar*) by men and women under the direction of a supervisor or master of weavers in a guild (*11*). On a smaller scale where the product was not intended for trading or export (*12*), women occupied their spare time at home with spinning and weaving.

In spinning, the carded wool (*napšu*) was drawn out from the skein (*kunšu*) and then spun with a clay or stone whorl to weight the spindle (*pilakku*) (*13*). This method was used not only with wool but with flax and cotton.

Rope made of wool was common in Babylonia. This was used to tie bundles of reed used instead of posts or beams to build the arched frame of reed huts for cattle (*14*). This rope also was used in the manufacture of *ḫuburu* jars (*15*). The caulker, boatswain, and rigging maker used wool in conjunction with other materials in boat making (*16*).

The usual procedure of the Babylonian before weaving was to remove most dirt in a wash pit (*17*) using some form of soap, potash, or alum (*18*). After weaving, the fuller trod it soundly in the fuller's pit to felt the woof threads (*19*), then he beat it with a club (*mazūru*) (*20*) and roughened it finally with thistles. The hot Babylonian sun was more than sufficient to bleach the materials.

VARIEGATED COLORS

The Mesopotamians were very fond of bright-colored clothes. In a Cappadocian tablet, an economic

Stone Dye Vats of the Eighth or Ninth Century B.C.

document, there are mentioned: "63 bright-colored (garments) for the clothing of servant boys" (*21*). The Egyptians pictured the people living to their east as being clothed in red and blue stripe and dot designs (*22*). In a hymn to the gods, the "robe of many colors" is mentioned (*23*). This coat of many colors was no doubt an early version of that later found in the Old Testament. In the Song of Deborah and Borak (*24*), it is described:

Do they not find and divide the spoil? For every brave man, a maiden or two, for Sisera, booty of dyed stuffs, spoil of varicolored dyed stuffs, two pieces of dyed material varicolored for my neck as spoil.

To achieve the variegated hues of their dress, the ancient Mesopotamians possessed not only substantive and vat dyes but also mordant dyes.

In describing the colors of the ancients it must be remembered that a sharp distinction between colors was not always made, *e. g.*, between yellow and green, red-purple and blue, and deep yellow and red (*25*, *26*). The entire color nomenclature is unclear. Nor is it clear as to how the ancient Mesopotamians used the known dyes since no procedural texts on dyeing have as yet been discovered. The dyeing materials are therefore not arranged in a more revealing order according to whether they are substantive, adjective, or mordant dyes. Wherever possible, however, evidence for their nature will be given. Some dyes and their colors are described here. No attempt has been made to list all of them, but only a few have been discussed to give a brief general picture bearing on the technological status of the ancient Mesopotamian dyeing industry.

NATURAL COLORS

White, black, brown, and gray, the natural wool colors, were probably the most common (*27*). Dyed thread and cloth were very expensive and were often found as important items of spoil as, for example, in the account of booty taken by Tiglath-Pileser III from Merodachbaladan on the Persian Gulf in the first millenium B.C. (*28*). The gray color was spun by "the smart women from white wool and black wool, spinning a double thread with the spindle, a brilliant thread, a large thread, a doubly dyed thread" (*29*).

Where the wool was to be dyed, the process was almost always carried out on the yarn or thread (*30*). In an Assyrian ritual text (*31*), black oxide of iron is put on a black thread, a red substance on a red thread, and iron (salt) on a blue thread.

Cassia bark, well known to the Sumerians, contains much tannic acid and when used with iron sulfate gives a black-green dye. Another black plant dye, from *Xanthium strumarium L.*, mentioned in Assyrian texts and at present growing near Basra, produces a gall-like substance (*32*). In the same category is the sumach plant (^{šam}*LID.GAS*) which, with ferrous sulfate, produces a black color on cotton or wool.

BLUE

Wool dyed blue (*33*) was very popular in Mesopotamia, particularly for garments (*34*). Among the items listed as tribute of the city of Qalparunda are "silver, gold, tin, horses, cattle, sheep, blue wool, and linen garments" (*35*).

The most famous and important of all blue coloring substances from time immemorial has been indigo. Thompson believes that ^{šam}*lalangu* may indicate the indigo plant. Three species of *Indigofera* are at present found in Syria and Palestine.

The indigo may be prepared in contact with lime or perhaps soda or potash (*36*). In a dye plant found at Tell Beit Mirsim, Palestine, of the eighth century B.C., a jar of lime was found together with a jar which contained "light gray ashes," probably potash. In view of the fact that an analysis had not been made for indigo in the vats found in the same room, it would be premature to conclude that this was an indigo dyeing plant, although vat dyeing was well known at this time.

Woad, *Isatis tinctoria L.*, is today found in Palestine (*37*). It was known to the Sumerians as ^{šam}*ZA.GÌN.NA*. Comparatively poor in coloring matter, woad must have necessitated much repetition of operations to achieve a dark blue.

YELLOW

Lighter colors seem to have been used infrequently in ancient Mesopotamia, judging by the relative scarcity of their citation in the texts. Saffron, a yellow dye, is obtained from the dried stigmas and tops of the styles of *Crocus sativus L.* In an Akkadian tablet, the clove of saffron is mentioned (*ṣupur a-zu-pi-ru*) (*38*). In Sumerian ^{šam}*ḪAR.SAG.SAR* is equivalent to ^{šam}*azupiru* from which we get the word saffron (*39*). Very dilute solutions of saffron must have been in use with the wet processing often repeated, since only one ounce of the dye is obtainable from 4300 flowers. In ancient times, saffron was probably more valuable in pharmacy where it was used extensively.

Turmeric, another yellow dye, obtained from the tuberous root of *Curcuma longa L.*, was also in use as a drug. The root is prepared by cleaning and drying in an oven. Both turmeric and saffron were used in antiquity as condiments.

RED

There is no doubt that red was an extremely popular color in ancient Mesopotamia (*40*). It was rivaled only by the very scarce and expensive purple. Various grades of red cloth must have been known, since texts refer to red cloth of the "second grade" and "third grade" (*41*, *42*, *43*). A very old text of the early second millenium B.C., dating from *AMAR-Sin*, second year, states: "sheep as payment for dyeing cloth red has *Igi-dar* received from *Lu-*^{d}*sin*" (*44*). Wool was often dyed the color of blood (*45*) as the following quotation from approximately the beginning of the first millenium B.C. shows: "that man you shall dress in a *šaḫḫū*-cloth, spread iron ochre on his temples, let its 'blood' flow." Red garments were used by the Assyrian priesthood and soldiery (*46*). The red garment was used both as an instrument of terror and as an exorcistic material (*47*).

Thompson describes three different shades of red found in Sumerian and Akkadian texts as blood red, rose color, and russet (*48*). It is probable that many

more shades of red were known to the Mesopotamians.

The dyeing of wool prior to plucking or shearing is frequently done in the Near East today. It is believed that the ancients practiced this procedure to some extent. In a Nuzi tablet of approximately 1300 B.C., there is the reading: "sheep whose red-dyed wool has been plucked *X*-times" (*49*). In a list of sheep, another Akkadian text reads: "five lambs whose wool is for dyeing," evidently before plucking (*50*).

Although madder has been found as a dye on the cloth wound about Egyptian mummies, no evidence for its use in Mesopotamia has yet been uncovered. In fact, there is no known word in Akkadian or Sumerian for madder.

The most important red dye, known to the ancient Babylonians was kermes (from the Arabic *qirmis*). It has been surmised already that kermes was obtained from the oak on the basis of philological evidence. In a lexical text, "red worm" is equated with "red drug of the thicket" (*51*). Another substance, a "drug for dyeing" mentioned in a text with oak-manna, may well refer to kermes (*52*).

A text from Nuzi of approximately 1300 B.C. seems to complete the evidence for the use of kermes and reads as follows (*53*):

> One woman of the palace for five talents of copper, Ili-ittiya, the merchant, took. And on the arrival of his caravan, for the five talents of copper (the equivalent) in cedar, cypress, tamarisk, (and) myrtle wood, in *X* and *X*, in blue and red-purple wool, and in rouge extracted from worms Ili-ittiya shall produce and in the palace to Taya deliver. Seal of Ili-ittiya, the merchant.

It may be noted that the source of cedar wood was Syria. The contract stipulates that the merchant pay the purchase price of the woman slave when the caravan returns. This document is interesting for another reason in that it uses the word for Canaan in the sense of red-purple, adding evidence that the word Phoenician came originally from the Greek word for "blood-red" (*phoînix*). In other words, the ethnicon is traced to the name for the dye and not vice versa as is ordinarily believed (*54*).

PURPLE

From the earliest Sumerian period, purple (*ŠIG ZA.GÌN.NA*) has been known (*55*). On an Assyrian prism fragment of the time of Sargon II, violet-purple and red-purple dyed wool are mentioned.

The most costly dye of antiquity was made from the gland of mussels found on the Phoenician and Cretan coasts and also on the beach at Sidon. The gland is in the shape of a small sac behind the head. It contains a very small portion of a colorless creamy fluid with a strong garlicy smell. On exposure to light, when applied to cotton or wool, it successively becomes green, blue, red, deep purple-red, and with washing in water and soap, a bright crimson (*56*). Two species were used, *Murex brandaris*, the commoner one, and *Murex trunculus* (*57*). These two species were probably mixed to attain the desired purple.

To prepare the juice of the Murex gland, it was salted, cooked for some time, put in the sun, and then evaporated until the proper intensity of color was obtained (*58*). From 12,000 mussels only about 1.5 g. of dyestuff is obtained (*59*). Wool was steeped in the dye solution until the proper shade was obtained.

It is, perhaps, of significance that purple dyestuffs are seldom mentioned in Sumerian and Akkadian economic documents. A rare mention is in an important text where *šamḫaza(l)lunu* is used in iron and pomegranate. If the Syriac *ḫalāzūnā*, Murex, is equivalent to *šamḫaza(l)lunu*, then this may be a recipe for dyeing purple with Murex and mordanting with iron and pomegranate rinds, according to Thompson (*60*). It is of course possible, but corroborative texts should be found before the metathesis postulated is accepted.

It is highly probable that most of the purple wool and cloth used by the Sumerians and their successors was imported from Syria as the evidence from an already discussed Nuzi text has shown. Syria's dyeing industry was well known. It is interesting that Sargon, with facetious contempt, when he captured Ilubidi of Hamath not far from Carchemish, North Syria, dyed his skin red. Sargon perhaps had the local dyeing industry in mind.

Cudbear, well known to the ancients, yielded a rich and beautiful purple. A combination of red and blue may have been used but the evidence is not available to bear this out.

PROCESSES IN DYEING

Owing to the meager evidence relating to the methods and operations for dyeing in ancient Mesopotamia, it may be instructive to refer back to the contemporary technology. Since leather manufacture and dyeing technology are closely related, it would be appropriate to examine the tanning and leather dyeing operations. In a first millenium B.C. tablet (*61*) we read:

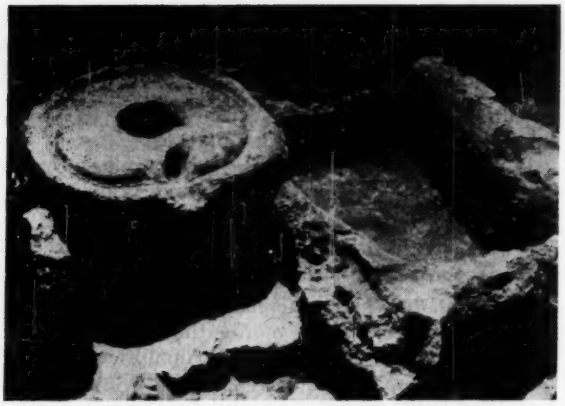
> *X* minas and six shekels of alum
> *X* minas of *pagratu* (gall)
> ½ *qa* of fat, ⅓ mina and two shekels of myrrh for tanning
> eleventh day of the month of Aiaru
> for Kidinnā
> worker in hides, having been curried
> the sixth day of Aiaru
> third year
> of Cambysus
> king of Babylon, king of the world

Closely resembling this text is a ritual recipe for tanning (*62*):

> You will take this hide and steep it in crushed flour of pure barley, in a solution of beer and first quality wine. With the best fat of an unblemished young bull, with alum of the Hittites and with gall-nuts, you will press it. Then you will spread it over a kettle-drum of brass.

In both cases, fat, alum, and gall are utilized. Mordanting is certain to have been fully established as an art much before the period of this tablet.

From the Talmud, which often reflects the Babylon-



Dye Plant Showing Rectangular and Circular Stone Vats

ian technology of the first millenium B.C., we know that wool was steeped in an extract of bran before dyeing (*63*). It was then placed in a copper kettle and warmed gently with the dye and the pulverized dry material (mordant?) (*64*). It was stirred by the dyer so that the dye would act evenly on the wool and not burn. Water was poured in (*65*). After a while, the wool was removed from the vat (*66*), washed, and dried (*67*). Often the wool was spotted and the job ruined.

DYEING APPARATUS

Mesopotamia proper has not as yet given up any dyeing apparatus to excavators. Important finds in Palestine of the eight century and earlier, however, have been made. At Tell Beit Mirsim, round stone vats were found, between 70 and 90 centimeters in height and in outer diameter, with the inner diameter between 30 and 45 centimeters and the mouth from one-half to one-third as wide. A circular groove was chiseled around the rims of the vats, with a connecting hole in the groove leading back to the vat. In some of the vats stones were still in place covering these holes. Albright believes that the circular groove was to catch the dye which then ran back to the vat through the small hole. The stone in the hole was to keep the liquid from splashing out (*68*). If analogy were to be made with later Arabic alchemical apparatus, the small hole was probably used primarily for sampling the solution and partly for brief stirring. When the dyeing was completed, the thread was probably unwound and removed by drawing it out through the hole. While the wound thread was in the dye, it was probably turned through the solution by a suspension work whose legs ran on the vat groove and in whose center was suspended the bobbin. It may be compared to a wagon wheel with the bobbin as an extension of the hub and with the rim revolving on the vat groove.

Other containers were found at Tell Beit Mirsim in the dyeing sectors. In one room were found rectangular basins of stone and plaster about 65 centimeters deep, 1.3 meters long, and 0.90 meters wide. Also, a narrow bench was found with a large handleless jar set into it, 51 × 35 cm. Near the vats, in the room corners, were found two hole-mouth jars partly full of slaked lime. This pattern was repeated in part or in whole in other dye plants found in this region. Another room held a rectangular basin of stone, mortar, and plaster, approximately 1.8 m. × 8 m. × 55 cm. A narrow masonry workbench held some pottery and a large two-handled pitcher. The dye plants in Tell Beit Mirsim were located very close to cisterns since the dyeing process requires a great deal of water.

Somewhat similar round vats were found at Beth Shemesh, from about 1000 B.C. or a little earlier and used down to 589 B.C. In this city, the commonest industries from the tenth century B.C. on were the pressing of olives and wine manufacturing, not vat dyeing (*69*). Very few of these vats were found in this locality.

Since no vats of this type have been discovered in Mesopotamia, it is likely that wooden vessels were used there. This is shown in a tablet where wooden utensils (*giš-á*) are mentioned for the treating of woolen and linen garments (*70, 71*).

Evidence points to a high development of the dyer's art in very ancient times. In the Near East, wool, cotton, and linen were dyed, the former being by far the most common. Colors were not differentiated sharply, at least linguistically. Purple and varicolored cloths were the most favored. The most common colors were not the dyed but the natural shades of wool such as white, black, brown, and gray. Red, yellow, and blue were also well known. The dyeing processes as they were known to the Mesopotamians are still largely unknown to us. The little that is known comes from the Talmud and from analogy with a few Babylonian tablets on tanning procedures. These probably had a common origin with the dyeing of fibers, or, more likely, preceded it in the remote prehistoric past. Dyeing of cloth was rare; the yarn or thread was put through the dye, usually in vats. Mordant dyeing, also very common, has already been demonstrated to have been in use in ancient Mesopotamia.

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SCIENCE PROJECTS—HELP FOR THE HELPERS

AN EXTREMELY valuable aid for teachers whose students are entered in science-exhibit competitions has recently come to our attention. It is "Science Exhibits," by Helen Miles Davis, published by Science Service, Washington 6, D. C. It should be on every high-school teacher's bookshelf. Two dollars buys these 90 pages of interesting reading for any chemist.

WEDGWOOD—A LIVING TRADITION

HENSLEIGH C. WEDGWOOD
Josiah Wedgwood & Sons, Inc., New York, N. Y.

THE utmost confusion seems to exist in regard to the different types of ceramic body, and no wonder. It all starts, of course, because we insist on describing ceramic ware generally as "china," when half the time the ware in question is something else. First of all, we want to enter a strong objection to calling all tablewares "china," when, as a matter of fact, other types of ware are involved as well. Would not the term "dinnerware" be more appropriate?

Anything made of baked clay, whether it be brick or porcelain, earthenware or bathtubs, is properly termed "ceramic," derived from the Greek, *Keramos*, "a pot." Because the Chinese produced a porcelain body, way back when, is no reason for calling anything ceramic by such a generic term as china—but it is done.

To try and make a little order out of chaos, let us first of all get firmly fixed in our minds that ceramic wares may be broadly classified into two distinct classes: (*a*) vitreous, or glassy in texture, and translucent, and (*b*) porous in texture, and opaque.

Class (*a*), the glassy kind, is properly called porcelain, the name being derived from the cowrie shell, which is glassy in appearance and was called *porcellana* by the Portuguese. Why porcellana? Because this shell looks rather like a miniature pig. This class includes both hard- and soft-paste porcelain, hotel china, and bone china.

Class (*b*) is properly called pottery and includes earthenware, faience, majolica, Queen's Ware, and that lower grade of earthenware dubbed by the department store with the horrible and meaningless term "semi-porcelain," which should be abolished.

The distinction between classes (*a*) and (*b*) is comparatively narrow, depending not only on raw material composition, but also on the degree of firing. There is also a large hybrid class between these two which may take on some of the attributes of both. To this class we may give the general term of stonewares; these include the following types, listed in descending order of hardness and porosity.

(1) Hard-glaze porcelain, such as French, German, or Japanese china.

(1) Soft-glaze porcelain, such as American china; and soft-glaze bone china, such as English china.

(3) Jasper and black basalt.

(4) Earthenware, both American and English.

(5) Earthenware, such as Mexican and Italian.

The difference in hardness of glaze between (1) and (2) is purely comparative and depends upon the fact that hard porcelain has a comparatively low first (or biscuit) fire and a very high glaze (or glost) fire, whereas American and English bone china receives the reverse treatment, *i. e.*, a very hard biscuit fire and a comparatively low glost fire. However, this is not to say that the low-fired glaze is not extremely hard and practical, for it is, and the only way of determining the difference between (1) and (2) glaze is to try scratching it with a steel file—and who wants to subject good dinnerware to such unnecessary tests?

Hard porcelain, American china, and English bone china are very similar in body composition, since all three contain kaolin (china clay), flint (or quartz), and a flux called Cornish stone which bonds these materials together. But whereas hard porcelain and American china use feldspar in addition, English bone china contains approximately 45 per cent bone ash.

Bone ash, being dead white, imparts a whiteness to bone china which the other classes lack, and it also gives great strength to the body. Furthermore, bone also adds a certain amount of plasticity to the body, which is made up for by the addition of a small proportion of white ball clays (plastic) in the case of hard porcelain or American china. Because of the use of feldspar in the hard porcelain and American types in contradistinction to English bone china, these two broad classifications are known as feldspathic china and bone china.

Both American and English bone china are translucent and nonporous, and there is little to choose between their hardness and "unchipability." The only great physical difference is that between an ivory and a white body.

Class (3), jasper and black basalt, are almost peculiar to Wedgwood, and the difference between classes (4) and (5) are so apparent that little needs to be said. Generally speaking, however, class (4) earthenware, as made by the English and American potteries, is cream in color and is harder fired than other types. Mexican and some American earthenwares are made from red- or buff-burning clays which are covered with engobes (liquid clay coatings) or colored glazes, which cover up the body color.

There is a tendency these days for the retail consumer to insist that she wants "real china," not always knowing what she really means. Admittedly, china has advantages over earthenware which it is not our intention to minimize. The customer, for instance, is aware that china is tougher than earthenware and will not chip as readily, and that, being as a rule more formal and certainly more expensive, her social position demands that she shall have "the best." But earthenware fills a great many other needs and, indeed, is

far more suitable than china in many informal homes. As a second set or as a starter in early married life, until a best china set can be afforded, earthenware is the answer; and indeed many people, once they have started with earthenware, will want to keep on using it because of its warmth and "friendliness," compared with the relative cold smartness of the more formal china.

It was Josiah Wedgwood who really perfected "cream ware" and put it on the market for all to buy. Building on the improvements of men like Thomas Astbury (died 1734), who introduced white clays and ground flints into the heretofore rather dirty-looking body, and Enoch Booth who, about 1750, introduced the liquid lead glaze, Wedgwood improved beyond all recognition the types of body which were being used before his time. By his improvements in the "body, shapes and glazes of the articles of our manufacture," he "converted a rude and inconsiderable manufacture into an Elegant Art and an important part of our National Commerce."

So great was this contribution to humanity that it was not long before all of his rivals and contemporaries in Staffordshire were making cream ware. It could be produced at such a price that all could afford it, in contrast to the state of affairs existing before his time when only the wealthy classes could afford to import Chinese porcelain or to use the limited supplies of Delft ware then available. Staffordshire cream ware became so popular and so widely known and used that it was used in every inn "from Moscow to Lisbon," and was also exported in large quantities to the Colonies in America before Josiah Wedgwood had been in business for more than ten years.

In 1765 Wedgwood was honored by a royal commission from Queen Charlotte, wife of George III, since which time with Her Majesty's permission, this cream-colored earthenware has been known as Queen's Ware.

Today Wedgwood's Queen's Ware is essentially of the same composition as the early cream ware, and consists of ball clay (for plasticity), china clay (for whiteness), ground burnt flint (for whiteness and strength), and Cornish stone (a fluxing material).

The secret of making porcelain never leaked out from the Orient, which, of course, was fine for the Chinese, who developed an extensive and lucrative export trade to England and Europe, and hence to America, throughout the seventeenth and early part of the eighteenth centuries. These export porcelains (which for some reason unknown are often dubbed erroneously with the name Lowestoft) were very often made to special order, decorated with armorial bearings. The Chinese kept their secrets, and their export trade thrived.

The result was not surprising. Imported porcelain was rare and costly and became so much prized that the European "philosophers" or alchemists, many of whom were maintained and supported by despotic European rulers with the main object of transmuting the base metals into gold, were told to quit trying to find the Philosophers Stone and to produce porcelain, or else!

The Elector of Saxony had a philosopher named Johannes Böttger whom he kept prisoner in the castle of Albrechtsburg. Here the wretched Böttger worked on his gold experiments, but at the same time carried on trials at reproducing Chinese porcelain. Actually, the fortunate man turned out to be successful in producing a fine red stoneware, and followed up this success in 1708 by finding a deposit of kaolin, which made possible the making of true porcelain. As a result of this success, the Elector established the famous porcelain factory at near-by Meissen.

Porcelains, and most other ceramic bodies for that matter, contain fluxes—that is, they must have a material which will melt in the fire and bond the other materials together. The more flux a body contains, the more it has a tendency to bond in the fire, and the more translucent it becomes. To get a good translucent, but at the same time rigid, body there must be a proper balance between the fluxes and the "rigid" materials.

Who discovered that calcined (burned) and ground bone would turn out to be such a perfect material for giving rigidity is open to question. It seems logical, however, that bone would do for a ceramic body what bones do for the human body. In Josiah Wedgwood's "Experiment Book," we find the record of early trials in which he used calcined bone.

Why is china more expensive? There are various reasons. In the first place, bone is an expensive ingredient (the best bones are considered to be the shin bones of oxen, most of which come from the Argentine). Second, china bodies are nearly always less plastic than earthenware. You cannot use such a high proportion of plastic ball clay in china because of its unfortunate property of giving an ivory color to the body. Because china body is so "short," it is very difficult to manipulate when it is being potted. Third, when dry, the china body is extremely fragile and will break at the slightest touch. Fourth, because of china's tendency to bend in the fire, plates have to be supported individually in fireclay boxes called "setters." Add to these the fact that patterns, at least in English bone china, are nearly always on-glaze enamels, requiring perhaps half a dozen hardening-on fires, and you can easily appreciate the fact that china is more expensive than earthenware.

Perhaps, though, in the long run it is *not*, because, as we have pointed out before, china is so much tougher and more chip-resistant that it will by far outlast an earthenware set in use.

Now for a word about china patterns. The same processes of decoration that are used on earthenware can be equally well applied to china, but in practice it is more common to find the decoration applied on-glaze. Because of the higher firing temperatures, the same kinds of limitations occur in the palette of usable colors as in the case of earthenware, only the palette is still more limited. China, furthermore, being considered

a greater luxury, demands a richness of decoration obtainable only by the use of on-glaze enamels and gold and platinum.

So where do we stand when it comes to the question: "Shall I buy china or earthenware?" Quite honestly, the question can be decided only by the buyer, having regard to her own tastes and to the use to which she intends to put her dinnerware. We have tried to present the pros and cons in an intelligent fashion, so that the purchaser may know both sides of the picture.

In summary, the advantages of china are that it:

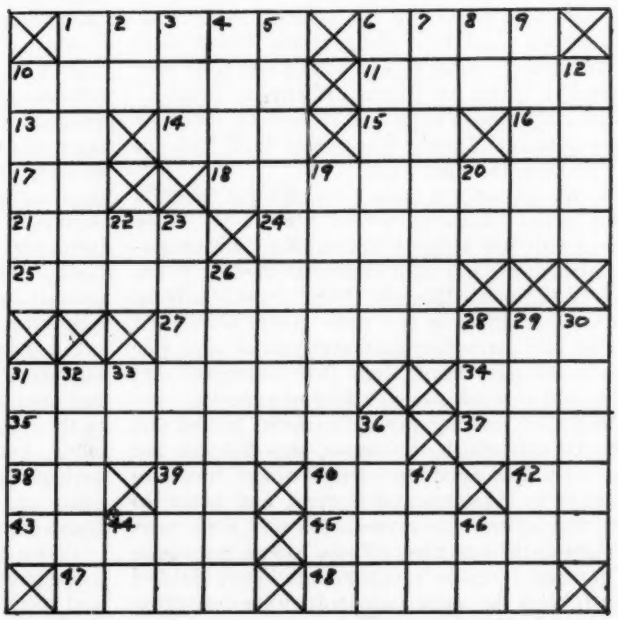
(1) is better for formal entertaining;
(2) is richer—looks more expensive;
(3) lasts longer;
(4) being vitreous, will not stain if chipped;
(5) will not craze.

On the other hand, earthenware is better in that it:

(1) is better for informal entertaining;
(2) is "warmer" in appearance;
(3) is less expensive;
(4) has underglaze colors that are more resistant to wear;
(5) is not so liable to crack, because of its better thermal expansion properties.

CROSSWORD PUZZLE

BERT H. CLAMPITT
Oak Ridge, Tennessee



Across

1. 0.238 calories
6. $CaCO_3$ is Iceland _____
10. The _____ effect of quantum mechanics
11. Eagles
13. Reagent (abbreviation)
14. I have
15. Sodium
16. A grandchild
17. Suffix denoting an alcohol
18. Eight-carbon acid
21. He built an ark
24. To fall in drops
25. $CaSO_4$
27. A camel
31. Propenyl-2,4,5, tri-MeO-benzene
34. English variant of she
35. Awakens a foul
37. Sun
38. Radium
39. Glucinium
40. Border of a garment
42. Dental technician (abbreviation)
43. Concur
45. Y_2O_3
47. SiO_2
48. A flower

Down

1. α Naphthoquinone
2. Preposition
3. Sodium is a _____ valent ion
4. Dextro and _____ rotatory
5. _____ are emitted by hot bodies
6. $(Fe, Mn, Pb)O \cdot TiO_2$
7. Swaggered
8. Article
9. Grease again
10. Sodium sesquicarbonate
12. A groom
19. $(CH_3)_2$—
20. All right
22. Exclamation
23. Gaseous element
26. Talked foolishly
28. Donkey
29. Rhodium in its highest valence state
30. Russian city where Roosevelt, Stalin, and Churchill met
31. Scent of flowers
32. Catches
33. 100 square meters
36. Combining form meaning bristle
41. Material
44. Radium
46. Sun god

(*See page 639 for solution*)

THE COMPOSITION OF THE ATMOSPHERE

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THE constituents of the dry atmosphere are given in most textbooks of chemistry in a form similar to that shown in Table 1. In one respect, such a table is no longer entirely adequate. To be sure, it includes the only four gases which are present in the dry atmosphere in more than trace amounts. However, to the knowledge of the author, such tables never distinguish among the various isotopic species of the gases concerned.

The interest in a table which would so distinguish lies in the fact that the heavy isotopes of oxygen and nitrogen are useful in chemical and biochemical investigations. The atmosphere is one source of heavy oxygen and is the sole significant source of heavy nitrogen.

TABLE 1
Composition of the Dry Atmosphere

	Parts per ten thousand (by volume)
Nitrogen	7809
Oxygen	2095
Argon	93
Carbon dioxide	3
All others	Traces

Such an important chemical resource is worthy of quantitative estimation.

Using the per cent isotopic composition of the elements concerned (which may be found in any handbook) and assuming random distribution of the various nuclides, it is possible to prepare Table 2, which takes isotopic composition into account. It is also possible to center attention not on molecules but on the nuclides themselves and to prepare Table 3. It is obvious from Tables 2 and 3 that the heavy isotopes of nitrogen and oxygen, while only minor constituents of the atmosphere, are far from being trace substances.

TABLE 2
Composition of the Dry Atmosphere by Molecular Species

	Parts per ten thousand (by volume)
$N^{14}N^{14}$	7753
$O^{16}O^{16}$	2085
A^{40}	93
$N^{14}N^{15}$	56
$O^{16}O^{18}$	8
$C^{12}O^{16}O^{16}$	3
$O^{16}O^{17}$	1.6
A^{36}	0.4
All others	Traces

Among the still rarer constituents of the atmosphere are the inert gases. Except for the helium occurring along with natural gas in certain wells, the atmosphere is the only significant source of these elements. The

TABLE 3
Composition of the Dry Atmosphere by Nuclides

	Nuclides per ten thousand nuclides
N^{14}	7818
O^{16}	2101
A^{40}	46.5
N^{15}	28.7
O^{18}	4.3
O^{17}	0.8
C^{12}	0.5
A^{36}	0.2
All others	Traces

TABLE 4
Inert-gas Composition of the Dry Atmosphere

	Parts per billion (by volume)
Argon	9,300,000
Neon	18,000
Helium	5000
Krypton	1000
Xenon	90

TABLE 5
Inert-gas Composition of the Dry Atmosphere by Nuclides

	Parts per billion (by volume)
A^{40}	9,260,000
A^{36}	32,000
Ne^{20}	16,300
A^{38}	5600
He^{4}	5000
Ne^{22}	1700
Kr^{84}	560
Kr^{86}	170
Kr^{82}	120
Kr^{83}	120
Ne^{21}	50
Xe^{132}	24
Xe^{129}	23
Kr^{80}	20
Xe^{131}	19
Xe^{134}	9
Xe^{136}	8
Xe^{130}	3
Kr^{78}	3
Xe^{128}	1.8
Xe^{124}	0.09
Xe^{126}	0.08
He^{3}	0.006

concentration of these gases in the atmosphere is given in Table 4, argon being included for the sake of completeness.

TABLE 6
Rare Molecular Species of Oxygen and Nitrogen in the Atmosphere

	Parts per billion (by volume)
$N^{15}N^{15}$	11,200
$O^{18}O^{18}$	830
$O^{17}O^{18}$	340
$O^{17}O^{17}$	30

The five stable inert gases listed in Table 4 are made up of a total of 23 different stable nuclides. Knowing the isotopic composition of the inert gases, Table 5 may be prepared in which the concentration of each nuclide is given.

The unit, parts per billion, was selected for use in Tables 4 and 5 because the volume of the atmosphere, calculated to 0°C. and one atmosphere pressure, is one billion cubic miles. It follows that a figure representing the volume of an atmospheric constituent as parts per billion also represents the volume in cubic miles made up by that constituent if it were collected in one place under those standard conditions of temperature and pressure.

Thus, there is enough Xe^{128} in the air, trace constituent though it be, to make up nearly two cubic miles of gas if it were collected in one spot. Even He^3, the least of the inert-gas nuclides, both in mass and in frequency of occurrence, would take up 0.006 cubic miles if collected which amounts to 24 billion liters or, in mass, 3.2 billion grams. In fact, even though He^3 occurs in the atmosphere only to the extent of six parts in a trillion, there is still enough of it for every cubic centimeter of air (at standard conditions) to contain 160,000,000 atoms of that nuclide.

One last note: There are species of oxygen and nitrogen molecules whose occurrence in the atmosphere is of the order of rarity of the inert gas nuclides. These, naturally, are the molecules made up entirely of the rarer isotopes of these elements (see Table 6).

THE EXPERIENCE OF A TECHNICAL SUMMER EMPLOYEE IN INDUSTRY

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LAST summer I had an opportunity to work with the Standard Oil Development Company in their Esso Research Center at Linden, New Jersey. The Standard Oil Development Company has, from time to time, conducted a limited program of summer employment for science teachers at the Esso Laboratories. While this has been confined mainly to teachers from universities having specializations pertinent to this company's activities, the program has also included high-school teachers. The Standard Oil Development Company is the central research, development, and engineering unit of the Standard Oil Company (New Jersey).

Obviously, the highly specialized nature of the activities limits the scope of the work which can be performed during a summer experience. It has, however, been possible to provide stimulating short-range projects. This permits a summer employee to do an entire job, giving him a feeling of pride in a completed work.

An experience of this nature helps teachers understand the free enterprise system by showing them how it works. Modern free enterprise is dedicated to serving people. By serving effectively it makes a profit, and the profit enables it to continue to serve. Teachers can be a powerful force in combating communism by explaining this philosophy to their students. Through the efforts of the public relations department and the company's operating divisions, the company has begun to answer the need for better understanding between education and industry.

THE WORK-TOGETHER PLAN

The company believes that it can help teachers to offer a more helpful type of school and university program by introducing them to the philosophy of modern industry. At the same time the company wishes to foster good relations among the schools, industry, and the general public. Teachers can sell the American way of doing things to the younger generation only if they themselves are completely familiar with it. In-

dustry is a big part of our American way and must therefore do its part in keeping the public informed concerning its operation; it believes that our method of free enterprise must be publicized if we are to combat its opponent, communism. Teachers can effectively do this, and industry is interested in helping them.

PURPOSES OF SUMMER EMPLOYMENT

In organizing the work for the summer employee, the Standard Oil Development Company keeps a number of items in mind. Some of the more important ones are listed below.

(1) They want to help the teacher financially.

(2) They want to give the teacher a type of job that will not be strictly routine but rather one that will give the teacher a feeling of accomplishment and self-satisfaction.

(3) They want to introduce the teacher not only to company philosophy and policy, but to the philosophy of modern American industry in general.

(4) They want to introduce the science teacher to the methods of modern scientific industrial research, with the idea that the high-school science classroom is the place where interest in a scientific career can be stimulated.

(5) They want the teachers to contribute to the purposes of the company.

(6) They want the teacher to gain as much useful information as possible.

HOW IT HELPS THE TEACHER

Looking at these items from the teacher's point of view:

(1) The financial assistance enables the teacher to participate in this program, instead of working at a job unrelated to his field of interest.

(2) The teacher benefits by obtaining useful material concerning the mechanics involved in research and the philosophy of free enterprise. This material will be useful in the classroom.

(3) He acquires a feeling for the basic philosophy of modern industry and can talk more intelligently about its organization and goals.

(4) He gains experience that might be valuable to him in obtaining future summer employment.

HOW IT WORKED

An opportunity was afforded me to work in the company's Esso Laboratories-Products Research Division.

The work was planned so that the teacher was offered all of the tools of research. A specific problem was decided upon. It was left up to the individual to organize and carry out the experimental work needed to solve the problem. In my case the problem was to determine the effect that composition has upon various physical properties of semisolid petroleum products. Literature describing past work done on the problem and the physical equipment needed to perform the desired investigation was given to the teacher. Supervision was not forced upon the teacher, but it was given graciously when asked for. As a science teacher I began to realize how valuable a person who can express himself, both in writing and orally, is to modern industry, This was realized by participating in the frequent reviews of the work, by writing memoranda and reports concerning the work, and by preparing and giving a final oral summary presentation of results, for the benefit of other technical employees.

Several informal discussions introduced the teacher to the philosophy of modern American industry. A two-day orientation program (offered as part of an indoctrination program to new employees) gave the teacher an over-all picture of the oil industry, and of the Standard Oil Company's organization and philosophy. The program stressed the transition of industry from the old fashioned type of "dictatorship" to the modern co-operative system, where the employees work as a team. Management is just another part of the team, not the overseer. The company believes in America's free enterprise system. Its primary purpose is to help people by offering good products; by doing this it makes a profit so that it can continue to serve the people. An opinion survey made a few years ago by a national opinion research organization indicates that some teachers do not understand this new philosophy of big industry.

By obtaining an over-all view of the industry and yet being able to work on a problem in one particular group, the teacher is able to return to the school with a clear, complete picture of just what the scientific industries have accomplished and what their goals are. The science teacher can more honestly and effectively stimulate young students to continue in technical scientific training to prepare themselves for a field in which there is, and will be for some time to come, an extreme shortage of personnel.

The teacher is therefore helping himself and the industry, and of most importance, he is helping better to guide the future citizens of our country.

THE BEER-LAMBERT LAW AND THE COMBINATION OF PROPORTIONAL DEPENDENCES

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In a recent article in THIS JOURNAL[1] Lohman pointed out that Lambert's law and Beer's law are often derived separately and then combined without mathematical justification into the Beer-Lambert law. He then suggested a procedure for effecting the combination. A method described by Slifkin[2] for combining proportional dependences can also be applied to this case. However, since various similar situations (Boyle's and Charles' laws; law of mass action) are usually encountered by chemistry students before they have studied calculus, which is required by both these methods, it is well to realize that combinations of this sort can be accomplished in a much simpler manner.

One such method, for example, can be applied to the radiation absorption laws as follows. Lambert's law states that $A = k_1 l$ where A is the absorbance, l is the length of the light path in the solution, and k_1 is independent of l but varies with the concentration c. For constant l, k_1 is proportional to A. But for constant l, Beer's law states that A is proportional to c. Therefore k_1 is proportional to c for a given l. This is true with the same proportionality constant for every l, since k_1 cannot depend on l. Thus the combined law, $A = kcl$, follows.

Another elementary method, similar to one attributed to A. T. Lonseth by Willard and Diehl[3] can be stated in a more general way as follows. It is assumed that:

$$y = f(x_1, x_2, \ldots x_n) \tag{1}$$

and that, for each independent variable, x_i:

$$y = k_i x_i \tag{2}$$

where k_i is a function of all the independent variables except x_i. Division of equation (2) by the product of all the independent variables, $\Pi_1{}^n x_i$, gives:

$$\frac{y}{\Pi_1{}^n x_i} = \frac{k_i x_i}{\Pi_1{}^n x_i} \tag{3}$$

in which the right member manifestly does not depend on the one independent variable, x_i. But since this equation can be written for every x_i, the left member must be independent of all the independent variables; that is, it must be constant. Therefore:

$$y = k\Pi_1{}^n x_i \tag{4}$$

This demonstrates the general rule that a function of several independent variables which is proportional to each one separately when all the others are constant is proportional to their product.

The main virtue of the combination procedures which require calculus is their not inconsiderable value as mathematical exercises for more advanced chemistry students. Probably the most useful for this purpose is the one employed, for example, by Daniels[4] and Klotz,[5] which may be generalized as follows, beginning again with equations (1) and (2). From equation (1) the complete differential of y is:

$$dy = \sum_1^n (\partial y/\partial x_i) dx_i \tag{5}$$

From equation (2):

$$(\partial y/\partial x_i) = k_i = y/x_i \tag{6}$$

Substitution of these into equation (5) and division by y gives:

$$d \ln y = \sum_1^n d \ln x_i \tag{7}$$

Integration and removal of logarithms leads again to equation (4).

The detailed application of this method to the combination of the gas laws, $V_{T,P} = k_1 n$ (an extension of Avogadro's law), $V_{n,T} = k_2/P$ (Boyles' law), $V_{n,P} = k_3 T$ (Charles' law), serves as an excellent refresher for the mathematics of thermodynamics and fits in easily with the usual preliminary discussion of properties of matter and equations of state.

In the presentation of the Beer-Lambert law, however, it seems desirable to derive the combined law directly. The above rule for the combination of proportional dependences can conveniently be employed in the following manner. Consider a monochromatic light beam of intensity I passing through an infinitesimal thickness dl of a solution with a concentration c of absorbing centers. It is obvious, or at least reasonable, especially from the viewpoint of col-

[1] LOHMAN, F. H., J. CHEM. EDUC., **32**, 155 (1955).
[2] SLIFKIN, L., *ibid.*, **25**, 346 (1948).
[3] WILLARD, H. H., AND H. DIEHL, "Advanced Quantitative Analysis," D. Van Nostrand Co., Inc., New York, **1943**, p. 112. The author is indebted to Professor Harold Horan of St. John's University for directing his attention to this reference.
[4] DANIELS, F., "Outlines of Physical Chemistry," John Wiley & Sons, Inc., New York, **1948**, p. 671.
[5] KLOTZ, I. M., "Chemical Thermodynamics," Prentice Hall, Inc., New York, **1950**, p. 60.

lisions between photons and absorbing centers as described by Goldstein and Day,[6] that the decrease in intensity, $-dI$, should obey the following three separate laws:

$$-dI = k_1 I \quad (k_1 \text{ constant for given } c \text{ and } dl) \qquad (8)$$

$$-dI = k_2 c \quad (k_2 \text{ constant for given } I \text{ and } dl) \qquad (9)$$

[6] GOLDSTEIN, J. H., AND R. A. DAY, JR., J. CHEM. EDUC., 31, 117 (1954).

$$-dI = k_3 dl \quad (k_3 \text{ constant for given } I \text{ and } c) \qquad (10)$$

The reason for considering an infinitesimal thickness, dl, is to limit the decrease of intensity to an infinitesimal value so that I may be considered constant as required by equations (9) and (10). A finite l and an infinitesimal c could just as well have been considered. The combined form of these three statements, $-dI = kIcdl$, integrates to the combined law which includes the separate laws as special cases.

A FAIRY STORY FOR CHEMISTS[1]

ONCE upon a time there was a happy little particle family which lived down in the shade of a lithium atom. There was Papa Proton, Mama Neutron, the little 1*s* twins, and the youngest member of the family, 2*s*. Little 2*s* was a merry little fellow whose favorite pastime was spreading out and behaving like a wave, which caused his mother no end of worry. She had always had trouble finding him since the day he was delivered by Dr. Heisenberg.

One day Mama Neutron stuck her head out through the dotted swiss orbitals covering the window of their happy little nucleus and shouted, "Junior!" She always called 2*s* "Junior" because she couldn't remember his name. "Junior," she said, "you may play anywhere you please (as long as you fulfill the Schroedinger wave equation), but don't go near the fluorine atom. He is a horrible, mean, electronegative old ogre who loves to take little 2*s* electrons and chain them into 2*p* bonds."

"All right, Mama," said little 2*s*, and he went skipping merrily up the energy levels in the garden behind the nucleus. It was a wonderful day and 2*s* was so full of energy ($h\nu$) that he gamboled about emitting childish ultraviolet waves of joy.

Suddenly little 2*s* felt a tug at his probability function. There leering over the garden was the fluorine atom. "Come into my 2*p* level," said the fluorine atom to the trembling little electron, meanwhile kicking another unfortunate electron back to its orbital. "You'll have lots of little playmates there." And before he knew it, little 2*s* found himself snatched away screaming as the fluorine ion (now atom) went racing down the road chortling to himself.

Suddenly the fluorine ion stopped short. On the path ahead was a beautiful, irresistably obvious member of the opposite sex. "Hi, Big Boy," she said. "Come up and see me some time. Just try the third electrolytic vat on the left and ask for Anne."

Little did the fluorine ion know, but this was the little electron's fairy godmother, Anne Ode, who just happened to be speeding down the path in her cadmium hot-rod.

The fluorine ion felt irrestibly drawn by her magnetic personality. "You and I could emit beautiful spectra together, baby," he said, pushing his eyes back in and straightening his 2*p* orbital.

"To coin a phrase, I bet you tell that to all the cute little electrodes," rejoined Anne.

All at once Anne noticed something strange about the fluorine ion. "My, what big orbitals you have. Have you been indulging in stray electrons again, in spite of my warning?"

The fluorine ion was caught red (7500 Å.) handed. Suddenly he made a break for it, but too late. The fairy godmother was too quick for him. With a wave of her magic wand (a reconverted Mohr buret) she freed the little electron and the fluorine ion was whisked away into a platinum cell at the top of an extremely high mountain of a very hard vacuum. There he was left all by himself to meditate on his crimes for the next megacentury.

And so, dear children, if someday you are slaving away in your laboratory over a hot test tube and you find a lithium atom which won't react, look very closely at it. You will see Papa Proton, Mama Neutron, and three little electrons sitting on the front porch of their happy little nucleus, and you will notice that little 2*s* always stays near at hand, because he promised never to stray away from home again.

Moral: Never kidnap an electron; it may be a shocking experience!

[1] [EDITOR'S NOTE: We wish we knew the source to be acknowledged for the above. We felt it was too good to keep from our readers. It is printed with the hope that the author may rise from obscurity, take his bow, and maybe even contribute again more directly.]

TEXTBOOK ERRORS[1]

V: The Reaction of the Leclanché Dry Cell

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PROFESSOR W. K. WILMARTH has suggested the consideration of the mechanism of the Leclanché dry cell for inclusion in this series. Descriptions of this still occasionally[2] include the reaction of manganese dioxide depolarizer with hydrogen gas. A check with some of the modern original literature revealed, interestingly enough, that most other textbook statements do not give the correct picture either.

The Leclanché dry cell is formed, as is well known, by zinc metal, an immobilized concentrated solution of ammonium and zinc chlorides, and a cathode mass of compressed manganese dioxide and carbon powders in contact with a carbon electrode.[3] That zinc dissolves at the anode is not questioned. But what happens in the cathode mass and in the electrolyte?

A cell reaction based on the formation of hydrogen gas in any significant concentration could lead only to e. m. f.'s of less than one volt. This would correspond to the E^0 difference between the zinc and hydrogen electrodes (0.76 volt) plus an amount which may be accounted for by the complexing action of chloride on the Zn^{++} ions or reduced by an amount due to the low concentration of H^+ ions in the solution. On the other hand, a calculation which includes the E^0 for the reduction of MnO_2 (about -0.7 volt[4, 5]) readily explains the actual values of nearly a volt and a half.

The question of what occurs at the cathode does not seem to have a complete answer at the present time, nor can the answer be a simple one because of the wide variety of conditions under which the cell is normally discharged. These may range from trickle discharge over a period of months or years to complete discharge in a matter of hours. In the former, diffusion may maintain approximately constant conditions throughout the electrolyte; in the latter, concentrations may vary tremendously within the cell. Cahoon and Heise[6] measured the pH in various parts of a cell which had been discharging for nine hours through a resistance of four ohms and found values varying from 3.8 near the zinc anode to 10.1 near the carbon electrode. This clearly demonstrates that the H^+-ion concentration can differ by a factor of over a million within a rapidly discharging cell. Obviously other, slower-diffusing ions may show gradients of the same order.

Under equilibrium conditions, when the Zn^{++} ion is able to diffuse to the cathode, the cell product appears to be a zinc manganite, $ZnMn_2O_4$ or $Mn_2O_3 \cdot ZnO$, identical with the mineral hetaerolite. This has been identified by X-ray diffraction[7, 8] in discharged cells and also has been found to be the stable phase formed from MnO_2, Mn^{++}, and Zn^{++} upon addition of base.[4] Under equilibrium conditions the cell reactions are therefore:

$$\begin{aligned} 2MnO_2 + Zn^{++} + 2e &= ZnMn_2O_4 \\ Zn &= Zn^{++} + 2e \\ \hline 2MnO_2 + Zn &= ZnMn_2O_4 \end{aligned} \qquad (1)$$

and there is no change in the electrolyte.

However, when equilibrium is not attained, the main reduction product seems to be the hydrous manganic oxide MnO(OH) or $Mn_2O_3 \cdot H_2O$, identical except for poor crystallization with the mineral manganite.[4] The cathode reaction is:

$$MnO_2 + H_2O + e = MnO(OH) + OH^- \qquad (2)$$

and the solution becomes alkaline in this region.

The OH^- can react with the NH_4^+ ions present to form NH_3, and both OH^- and NH_3 can react with Zn^{++} ions to form amines and basic salts. Depending on initial conditions and rates of formation and diffusion, different products appear. Under moderate currents an insoluble diamine chloride $Zn(NH_3)_2Cl_2$ precipitates and cements the cathodic mixture to a hard mass.[6] The over-all cell reaction could then be written as:

$$2MnO_2 + Zn + 2NH_4^+ + 2Cl^- = 2MnO(OH) + Zn(NH_3)_2Cl_2 \qquad (3)$$

The electrolyte becomes depleted in ammonium chloride

[1] Suggestions of material suitable for this column are eagerly sought and will be acknowledged. They should be sent with as many details as possible to K. J. M. at the above address.

[2] Since the purpose of this column is to prevent the spread and continuation of errors and not the evaluation of individual texts, the source of the errors discussed will not be cited. The error must occur in a least two independent standard books to be presented.

[3] For a brief review of the evolution and variations, see HEISE, G. W., AND N. C. CAHOON, *J. Electrochem. Soc.*, **99**, 179C (1952).

[4] MCMURDIE, H. F., D. N. CRAIG, AND G. W. VINAL, *Trans. Electrochem. Soc.*, **90**, 509 (1946).

[5] CAHOON, N. C., *J. Electrochem. Soc.*, **99**, 343 (1952).

[6] CAHOON, N. C., AND C. W. HEISE, *Trans. Electrochem. Soc.*, **94**, 214 (1948).

[7] COPELAND, L. C., AND F. S. GRIFFITH, *ibid.*, **89**, 495 (1946).

[8] MCMURDIE, H. F., *ibid.*, **86**, 313 (1944).

and stays neutral or, more precisely stated, as much acid appears near the anode as there is base produced near the cathode.

Under very severe drainage conditions the amount of ammonia formed in the cathode exceeds the amount of zinc present, and higher amines, such as the tetramine ions, are formed. Their hydrochlorides are relatively soluble and no precipitation occurs.[6] The cathode mixture remains friable but develops a strong odor of ammonia. The over-all cell reaction now becomes:

$$2\,MnO_2 + Zn + 4NH_4^+ = 2MnO(OH) + Zn(NH_3)_4^{++} + 2H^+ \quad (4)$$

The over-all concentration of acid in the electrolyte increases. More precisely stated, there is more acid produced near the zinc anode than there is base appearing in the cathode mass.

Under some conditions, probably when the concentration of Zn^{++} is high[9] or when ammonia becomes locally depleted through precipitation of the diamine[6] (equation (3)), a basic chloride $ZnCl_2 \cdot 4Zn(OH)_2$ precipitates.[8] The cell reaction then can be represented:

$$8MnO_2 + 4Zn + Zn^{++} + 2Cl^{--} + 8H_2O = 8MnO(OH) + ZnCl_2 \cdot 4Zn(OH)_2 \quad (5)$$

The electrolyte becomes depleted in zinc chloride and, on the whole, remains neutral.

This over-all picture seems too complicated for presentation to most freshmen. Which part of it should be presented, with proper reservations, is a matter of taste. Since most of the general discussion of cells at that level deals with reversible phenomena it would seem logical perhaps to present equation (1) (with formation of hetaerolite) and mention that under more severe usage conditions other products and reactions become important.

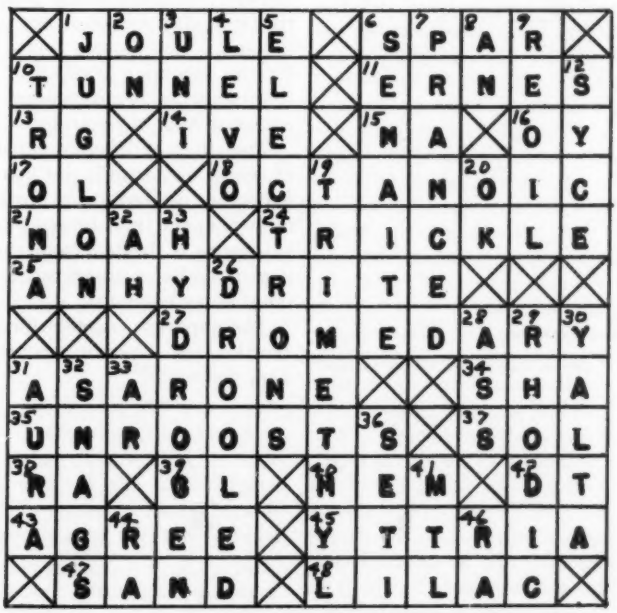
It might be noted incidentally, that the term "dry cell" has become highly ambiguous in the last dozen years or so. While the Leclanché cell remains the most important dry cell there are others that are well established such as the mercuric oxide,[10] the alkaline MnO_2,[11] or the magnesium[12] dry cells.

[9] DANIELS, F., *ibid.*, **53**, 45 (1928).

[10] BOOE, J. M., *J. Electrochem. Soc.*, **99**, 197C (1952).

[11] HERBERT, W. S., *ibid.*, 190C.

[12] MOREHOUSE, C. K., *ibid.*, 187C.


J O U L E S P A R
T U N N E L E R N E S
R G I V E M A O Y
O L O C T A N O I C
N O A H T R I C K L E
A N H Y D R I T E
D R O M E D A R Y
A S A R O N E S H A
U N R O O S T S S O L
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A G R E E Y T T R I A
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Solution to Crossword Puzzle on Page 632

APPARATUS FOR THE DEMONSTRATION OF CONDUCTIVITY OF ELECTROLYTES

HANS A. SUTER[1] **and LORRAINE KAELBER**
Rollins College, Winter Park, Florida

THE usual apparatus for the demonstration of the electric conductivity of aqueous salt solutions consists of a small flask or a test tube into which is placed the solution to be examined, and two metallic conductors which are dipped into the solution. If the solution contains an electrolyte the gap between the conductors is short circuited and the flow of current can be detected by suitable means, *i. e.*, by the lighting up of a light bulb.

In order to show the effect of different compounds or the effect of dilution on conductivity, either a series of flasks is necessary or the flask has to be emptied and refilled with the new solutions. This procedure is not only cumbersome, but the continuous, gradual decrease of conductivity of salt solutions with dilution is difficult to show effectively.

The apparatus which is described below is very simple and readily assembled and does not have the disadvantages mentioned above. Furthermore, it is believed that it shows the conductance by electrolytic solutions much more impressively than does the usual setup.

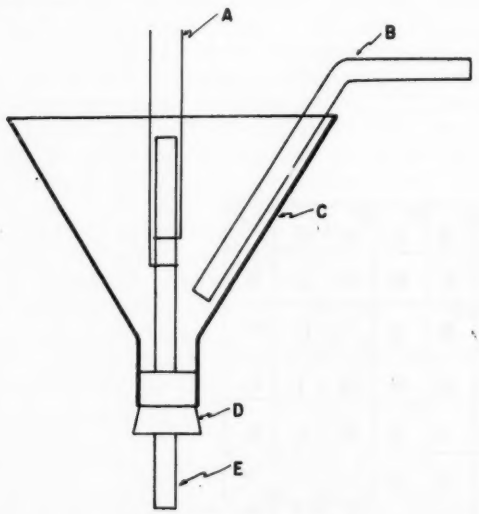
The apparatus is shown diagrammatically in the figure. The center glass tube serves as the drain. On the portion of this glass tube inside the funnel are wound two lengths of copper wire. The proper distance between these two loops is determined by the conductivity of the local tap-water supply. The wires are connected to an electrical plug in series with a light-bulb socket. The funnel is supported by an iron ring secured on a ring stand and the water inlet tube is held by a buret clamp.

To show electrolytic conductivity the water is turned on and allowed to flow at a moderate rate through the funnel, and the plug is connected to an a.-c. outlet. The light bulb should not light up if the gap between the two copper leads is properly adjusted. The addition of a small quantity of an electrolyte, such as sodium chloride, to the flowing water in the funnel will light the lamp after a short interval required for dissolution of the salt. As the salt solution is diluted continuously by the incoming water the light intensity decreases, thus showing the dependence of conductivity on the concentration of electrolyte.

The effect of different substances on the conductivity of water can readily be demonstrated by adding any substance desired to the flowing water in the funnel and observing the light intensity of the bulb. As soon as a substance is flushed from the funnel a new compound can be added without any manipulation of the equipment being necessary.

The apparatus as described was designed as a demonstration for a public science show and proved to be very successful.

[1] Present address: Celanese Corporation of America, Clarkwood, Texas.



Conductivity Apparatus

A, copper wire; *B*, water inlet; *C*, powder funnel; *D*, rubber stopper; *E*, water drain.

THE INTERMEDIATE COURSE IN CHEMISTRY

W. C. VOSBURGH, PELHAM WILDER, JR., and J. H. SAYLOR
Duke University, Durham, North Carolina

QUALITATIVE analysis was originally taught as a part of the analytical chemistry course. As it has declined in practical importance, the conventional qualitative analysis course has been dropped from some curricula and in others its emphasis has been changed. The main concern of the theoretical part is now the physical chemistry of water solutions. It is recognized that the laboratory work of qualitative analysis gives experience in a large number and variety of reactions which illustrate some important theoretical principles.

Over ten years ago one of the authors devised and tested with a small class a set of experiments that he hoped would better illustrate solution chemistry. The greatest change was to make some of the experiments quantitative. The revised program seemed successful and it was adopted for all students in the first semester of the second year of chemistry. Entitled "Fundamentals of Analytical Chemistry," this course has been in operation since then; the instructors concerned have found it to be superior to a laboratory program consisting wholly of qualitative analysis.

GENERAL ORGANIZATION

Fundamentals of Analytical Chemistry follows one year of general chemistry, in which two-thirds of the second semester's laboratory work is devoted to qualitative analysis. The course carries four semester hours credit and consists of one lecture, one recitation period, and two three-hour laboratory periods per week. The lectures treat the standard material and problems in elementary solution theory and are illustrated where practicable by lecture demonstrations. The recitation sections are devoted to informal discussions of the previous lecture and the material and problems assigned from the text; written quizzes are given frequently.

About 160 students enroll for the course each year. An average class is composed of 15 per cent chemistry majors, from six to eight per cent majors in other scientific disciplines, and 75 per cent premedical students.

LABORATORY PROGRAM

The objective of the laboratory program is to illustrate theories and reactions of solutions of electrolytes. A number of the experiments are quantitative because it is felt that an understanding of the quantitative aspects of the theories is important. These experiments constitute an introduction to the methods of quantitative analysis. Three experiments are of the conventional qualitative analysis type, since these procedures and reactions contain many good illustrations of electrolyte theory.

The 11 experiments completed during a semester are described below.

(*1*) *Weighing.* The student is taught how to use and care for the analytical balance and to weight to the nearest milligram. Here as in the other experiments, the principle is stressed and precision is sacrificed to speed and convenience. The maximum precision required in any experiment is one part per hundred (one per cent).

(*2*) *Preparation and Standardization of a 0.5 M HCl Solution.* A solution of approximately 0.5 *M* HCl is standardized gravimetrically by weighing silver chloride. The use of a pipet, the technique of weighing a precipitate, and the significance of a standard solution are taught.

(*3*) *Determination of the Concentration of an Unknown $NaHCO_3$ Solution.* The fundamental concepts of volumetric analysis are illustrated by titration of a measured volume of unknown $NaHCO_3$ solution with the standard HCl solution prepared in Experiment 2. The definition of concentration in terms of both grams per liter and moles per liter is stressed. In the titration the buret is read to the nearest 0.1 ml.

(*4*) *Properties of Electrolytes.* This consists of a number of qualitative, test tube experiments, directed toward an understanding of the chemical nature of solutions of electrolytes.

(*5*) *Colorimetric Determination of Copper.* This experiment illustrates the relationship between the color of a solution and the concentration of the colored solute, in preparation for use of the colorimetric method in later experiments. The copper-ion concentration in an unknown solution is found by the addition of ethylenediamine to a measured sample and determination of how much of a known solution treated in the same way is required to match the color. The color comparison is made visually with matched test tubes but without an instrument.

(*6*) *Ammonium Sulfide Group of Qualitative Analysis.* The analysis of this group is carried out by the conventional scheme for the separation of the cations, and on a semimicro scale. The emphasis is placed on chemical principles and semimicro technique rather than on the teaching of an immediately practical analytical method. The ammonium sulfide group is placed before the hydrogen sulfide group in the laboratory schedule

[1] From a paper presented at the Southeastern Regional Meeting of the American Chemical Society, Birmingham, Alabama, October, 1954.

because of the greater experimental difficulties generally experienced by the student in the analysis of the hydrogen sulfide group.

(*7*) *Ionization Constants of Picric Acid and Dinitrophenol.* In order to help the student to connect the chemical equilibrium equation with the actual behavior of a system in equilibrium, the ionization constants of two weak acids are measured. The acids are chosen so that the fraction ionized can be measured by a simple colorimetric procedure.

The student first observes that the addition of a large excess of hydrochloric acid to picric acid destroys the yellow color by suppression of the ionization. In contrast, sodium hydroxide develops the full color by salt formation. The color is obviously that of the anion. Then solutions containing moderate excesses of strong acid are matched in color by alkaline solutions to which the required amounts of a known picric acid solution are added. The picrate-ion concentrations of the acid solutions are thus determined colorimetrically. The nonionized picric acid can be calculated by difference and the hydronium-ion concentration is set equal to the hydrochloric acid concentration. The ionization constant can then be calculated.

The ionization constant of 2,4-dinitrophenol or of 2,6-dinitrophenol is determined similarly. Because these are much weaker acids than is picric acid, the hydrochloric acid concentration required to give the common-ion effect is much smaller, and the hydronium-ion concentration must be taken as equal to the sum of the hydrochloric and ionized dinitrophenol concentrations.

(*8*) *Determination of the Ionization Constant of Acetic Acid by Colorimetric pH Measurements.* This experiment introduces buffer solutions, pH, indicators, and the colorimetric measurement of pH, as well as some new quantitative analysis methods.

A sodium hydroxide solution is prepared and standardized against the standard acid prepared in Experiment 2, and also against a 0.1 *M* potassium acid phthalate solution prepared by weighing the pure solid. Then an acetic acid solution is standardized against the sodium hydroxide solution and some of the latter is diluted to 0.1 *M*.

Two acetate buffers are prepared from the acetic acid and 0.1 *M* sodium hydroxide solutions, and a series of phthalate buffers from the 0.1 *M* phthalate and sodium hydroxide solutions. By means of methyl red indicator, the acetate buffers are compared colorimetrically with the phthalate buffers, of which the pH values are known. The ionization constant of acetic acid can be calculated from the compositions and pH values of the acetate buffers.

(*9*) *Hydrogen Sulfide Group.* This is similar to Experiment 6.

(*10*) *Solubility Product of Lead Iodide.* A further exercise in the application of the principles of chemical equilibrium to a real system is furnished by the precipitation of lead iodide, when solutions of lead nitrate and potassium iodide of known concentrations are brought together in varying proportions. By a simple experimental method it is found that the solubility of lead iodide is affected considerably by the presence of either lead nitrate or potassium iodide, but that in spite of variations in the separate ion concentrations the value of the solubility-product constant is approximately the same in all trials.

(*11*) *Qualitative Analysis of an Alloy.* A commercial alloy composed primarily of metals of the first three groups of the qualitative analysis scheme is analyzed for members of those three groups only.

DIVISION OF CHEMICAL EDUCATION

"DIRECTLY or indirectly the Division of Chemical Education is making a significant contribution to every member of the American Chemical Society. With its dynamic and continually expanding program, it is exerting a positive influence on American education."

This statement, quoted from the Division's 1955 Directory, makes plain the reason for the growth of its membership. Support of the Division is more than enjoyment of good programs at national meetings. The publication of THIS JOURNAL, organization and direction of summer institutes, the supervision of the A. C. S. cooperative examination program, and a variety of other activities involve the participation of hundreds of its members. Every member is on the "membership committee." Treasurer W. F. Ehret, New York University, receives the one-dollar dues.

The editors of THIS JOURNAL hope for the time when every name on the Division's roll will also be found on THIS JOURNAL's subscription list. They suggest that no more tangible support exists for belief in the importance of training more and better chemists.

DIVISION OF CHEMICAL EDUCATION

OF THE AMERICAN CHEMICAL SOCIETY

Report of the Treasurer, September 1, 1955

DIVISION ACCOUNT

Receipts:		
Balance on hand 9/1/54	$ 1083.80	
From conversion of three Series G to four Series J bonds	12.00	
Final interest on three Series G bonds.	3.75	
Refund from National Office for unused postcards	4.43	
Return of unused funds by Comm. on Teaching College Chem. (O. M. Smith)	290.00	
Dues previous year	11.00	
Dues received	2117.00	
Total receipts		$ 3521.98
Expenditures:		
Bank charges (former treasurer)	$ 1.00	
Bank charges	6.90	
	7.90	
A. C. S.—New York meeting speaker and mailing separates	92.89	
A. C. S.—New York meeting separates	57.85	
A. C. S.—Cincinnati meeting mailing separates	77.44	
A. C. S.—Cincinnati meeting separates	26.06	
A. C. S.—Cincinnati meeting dinners for program comm.	24.63	
A. C. S.—Dues receipt cards	65.00	
A. C. S.—Division's share in printing uniform application forms	24.00	
	367.87	
Mailing directories and "Facts" Books	800.58	
Committees		
L. L. Quill, A.A.A.S. Cooperative	172.08	
O. M. Smith, Teaching College Chemistry	300.00	
J. F. Baxter, Institutes and Conferences	50.00	
	522.08	
President's office	220.33	
Secretary's office	153.05	
Treasurer's office	804.33	
Total expenses		$ 2876.14
Cash balance on hand 9/1/55		645.84

Assets distributed as follows:

Checking account—"Division of Chemical Education, Wm. F. Ehret, Treasurer"—First National Bank, Oradell, New Jersey	645.84
Four (4) U. S. Savings Bonds, Series J, at $100 ea., Nos. C160832–5J. Deposited with R. V. Mellefont, Treas., American Chemical Society	288.00
Total	$ 933.84

JOURNAL ACCOUNT

Balance on hand 9/1/54		
Bonds	$18,000.00	
Cash	8040.02	
Receipts:		
Chemical Education Publishing Co., Easton, Pennsylvania. Net transfer to JOURNAL fund from 1954 profits	1832.89	
Interest on bonds	362.50	
Interest on bank account	5.48	
Transfer of account from East Lansing, July 8, 1955	8370.92	
Total receipts		$10,571.79
Expenditures:		
Purchase of eight (8) U. S. Savings Bonds, Series K, at $1000 ea.		8000.00
Cash balance on hand 9/1/55		2571.79

Assets distributed as follows:

Savings account No. 2894, River Edge Savings and Loan Association, River Edge, New Jersey.	$ 2571.79
Seven (7) U. S. Savings Bonds, Series G, $1000 ea., Nos. M: 5560890G, 5560861G, 5560855G, 5560856G, 5560857G, 5560858G, 5560859G, deposited with Robert V. Mellefont, Treas., Amer. Chem. Soc., 1155 16th Street, N. W., Washington 6, D. C.	7000.00
Four (4) U. S. Savings Bonds, Series G, $1000 ea., Nos M: 5866176G, 5844177G, 5855178G, 5855081G (deposited with R. V. Mellefont as above)	4000.00
Four (4) U. S. Savings Bonds, Series G, $1000 ea., Nos. M: 7280064G, 7280066G, 7280067G, 7279936G (deposited with R. V. Mellefont as above)	4000.00
Three (3) U.S. Savings Bonds, Series G, $1000 ea., Nos. M: 7438009G, 7438010G, 7437661G (deposited with R. V. Mellefont as above)	3000.00
Eight (8) U. S. Savings Bonds, Series K, $1000 ea., Nos. M399072–9K (deposited with R. V. Mellefont as above)	8000.00
Total	$28,571.79

WM. F. EHRET, *Treasurer*

Report of the

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

SEVENTEENTH SUMMER CONFERENCE

THE Seventeenth Summer Conference of the New England Association of Chemistry Teachers was held August 15–20 at Tufts University, Medford, Massachusetts, with Roland M. Whittaker, Queens College, Flushing, New York, and Angela M. Trovato, Exeter High School, Exeter, New Hampshire, as co-chairman. The conference was welcomed to Tufts by Paul H. Doleman, acting chairman, department of chemistry. Robert D. Eddy, Tufts University, served as secretary of the conference committee. Clarence D. L. Ropp, University of Bridgeport, Bridgeport, Connecticut, ably assisted by Mrs. Ropp, undertook the time-consuming and exacting duties of the registrar-treasurer. Because of adverse publicity concerning the poliomyelitis epidemic in the Boston area, there were 22 cancellations, particularly of guests and family groups. In spite of this, 193 registered for the conference and enjoyed the excellent housing afforded at the new Carmichael Hall and the stimulating technical and recreational program.

Among those registered, as would be expected, New Englanders outnumbered those from more distant regions; but there were 52 of the latter from New York, Pennsylvania, Maryland, California, Florida, North Carolina, New Jersey, Ohio, Quebec, and the District of Columbia.

The following have attended all 17 Summer Conferences:

Mr. and Mrs. Grover C. Greenwood, Bridgeport, Connecticut (retired).

Mr. and Mrs. S. Walter Hoyt, Belmont, Massachusetts (retired).

Mr. Alfred R. Lincoln, Hampden College of Pharmacy, Willimansett, Massachusetts.

Miss Evelyn L. Murdock, Stonington High School, Stonington, Connecticut.

Miss Elsie Scott, Northfield School, Northfield, Massachusetts.

Dr. John R. Suydam, Boston, Massachusetts (retired).

For the first time at any summer conference, various sections of the American Chemical Society gave grants-in-aid. The Northeastern Section grants were named in honor of Lyman Churchill Newell, first president of NEACT. The following registrants were recipients:

Maine Section. John J. Kassay, Gardiner High School, Gardiner, Maine; James D. Marshall, Lawrence High School, Fairfield, Maine.

Northeastern Section. Nello A. Allegrezza, Milford High School, Milford, Massachusetts; Murray B. Hicks, Chelmsford High School, Chelmsford, Massachusetts; Joseph F. Walsh, Jr., Roxbury Memorial High School for Boys, Boston, Massachusetts; Richard M. Whitney, Roxbury Latin School, Boston, Massachusetts.

Connecticut Valley Section. John J. Prymak, Farmington High School, Farmington, Connecticut.

Western Connecticut Section. Richard M. Strawcutter, Greenwich High School, Greenwich, Connecticut.

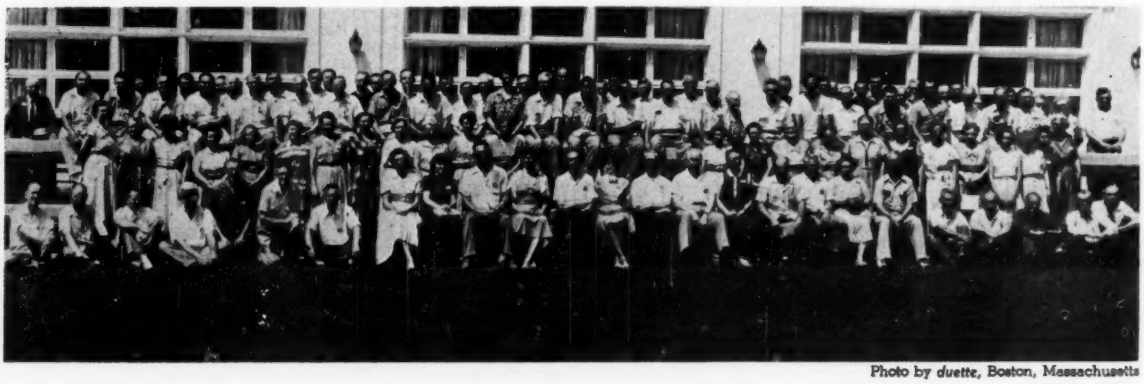


Photo by *duette*, Boston, Massachusetts

Maryland Section. Donald M. Rankin, Baltimore Junior College, Baltimore, Maryland.

The David L. Davidson award was won by John H. Walters, Browne and Nichols School, Cambridge, Massachusetts.

Tickets for the Boston Red Sox-New York Yankees baseball game at Fenway Park aroused surprisingly little interest when first announced. By the day of the game, however, when it looked as though this game might decide the championship, the committee was besieged with requests for unavailable tickets. The rains of "Hurricane Diane" began during the day but fortunately were miraculously interrupted long enough to permit a dry trip, first to the First Iron Works, Saugus, Massachusetts, and then to the ball game. The week started with fair but excessively hot weather and ended with a record rain of 14 inches in one day, but the planned program was carried through to the end. At the last session Ruth Ellis, professor of chemistry at Vassar College, showed colored slides and related her experiences during two years in India where she established senior chemistry courses at the Women's Christian College near Madras.

Because of the increasingly depressing weather, the guest activities gradually reduced to individual forays to near-by shopping centers and impromptu bridge games in the lounge. It was possible to visit Harvard, Massachusetts Institute of Technology, and the Boston Museum of Science. The historical walk in Boston never came to pass and the day at Crane's Beach was washed out. On the contrary, attendance at the technical talks was much better than average! The exhibits of equipment and textbooks, arranged by Thomas R. P. Gibb, Jr., of Tufts University, were very well attended.

The evening programs included an illustrated lecture on "K-2, the savage mountain," by Robert Bates of Phillips Exeter Academy, Exeter, New Hampshire. Raymond J. Spahr of Chicopee Manufacturing Corporation discussed and showed an interesting collection of non-woven fabrics. Charles J. Umberger of the Office of the Chief Medical Examiner, City of New York, gave a fascinating picture of the applications of scientific techniques in solving mysterious deaths in the five New York boroughs.

Henry E. Wendon of Tufts University and Harvard, exhibited a wonderful collection of models of crystal structures and demonstrated how to make them. Amateur photographers took advantage of the opportunity to make colored photographs of these complex models. Stuart S. Flaschen and Morgan Sparks of Bell Telephone Laboratories discussed piezo-electric crystals and transitors in very lucid talks, and George E. Henry of General Electric Company demonstrated applications of ultrasonics. Charles R. Dawson and Erich Hirschberg, both professors at Columbia University, discussed the toxic principle of poison ivy and experimental cancer chemotherapy, respectively. Educational topics were presented by Samuel Madras, Sir George Williams College, Montreal; Laurence S. Foster, Ordnance Material Research Office, Watertown Arsenal; and Henry Gabriel, Sienna College. Their papers will appear in the REPORT in THIS JOURNAL. The effects of nuclear radiations and blast from atomic bombs on preserved foods were reported on by C. A. Greenleaf of the National Canners Association. Co-chairman Whittaker was congratulated on his excellent program.

ADJOURNED ANNUAL MEETING, AUGUST 16, 1955

The adjourned annual meeting of the NEACT was reconvened at 10:30 A.M. by President Marco H. Scheer.

The treasurer's report was presented by Carroll B. Gustafson. An abridged statement follows:

Expenses for the year July 1, 1954, to June 30, 1955...	$2693.21
Receipts	2632.65
Deficit	60.56
Balance, July 1, 1943	1305.76
Balance, August 9, 1955	$1245.20

The deficit is more than offset by the income to the endowment fund which will be credited to the 1954–55 income account.

Leallyn B. Clapp, secretary, presented the report of the membership committee. The final membership figure on June 30, 1955, was 569. The following members have joined since the May meeting:

Fred W. Anderson, Chemistry Teacher, North Haven High School, North Haven, Connecticut.
Frank P. Perrone, Teacher of Physics and Chemistry, Dorchester High School, Dorchester, Massachusetts.
Mrs. S. W. Prentiss, Chemistry Teacher, Westover School, Middlebury, Connecticut.
John J. Prymak, Head of Science Department, Farmington High School, Farmington, Connecticut.
Robert W. Sullivan, Head of Chemistry Department, Lawrence High School, Lawrence, Massachusetts.
Hugh Templeton, Superintendent of Science Education, New York State Department of Education, Albany, New York.

The following members joined at the Seventeenth Summer Conference or immediately thereafter:

Nello A. Allegrezza, Instructor, Milford High School, Milford, Massachusetts.
John F. Baxter, Professor of Chemistry, University of Florida, Gainesville, Florida.
Wallace J. Gleekman, Head of Science Department, Wrentham High School, Wrentham, Massachusetts.
Murray B. Hicks, Science Instructor, Chelmsford High School, Chelmsford, Massachusetts.
James D. Marshall, Science Department, Lawrence High School, Fairfield, Maine.
John B. Martin, Science Teacher, Rutland High School, Rutland, Vermont.
Stuart A. Mayper, Assistant Professor of Chemistry, Brandeis University, Waltham, Massachusetts.
Dorothy Merrill, Science Teacher, Hanover High School, Hanover Center, Massachusetts.
Maryalice Moore, Science Teacher, Taunton High School, Taunton, Massachusetts.
Thomas J. Murphy, Jr., School Department Representative, McGraw-Hill Book Company, New York, New York.
Charles N. Ott, Department of Chemistry, Guilford College, Guilford College, North Carolina.
Merle F. Showalter, Associate Professor of Chemistry, North Carolina State College, Raleigh, North Carolina.

Paul C. Staples, Science Teacher, Templeton Junior High School, Baldwinsville, Massachusetts.
Joseph F. Walsh, Jr., Chemistry Teacher, Roxbury Memorial High School, Roxbury, Massachusetts.
Richard M. Whitney, Head of Science Department, Roxbury Latin School, West Roxbury, Massachusetts.
Harold Zallen, Science Teacher, Senior High School, Natick, Massachusetts.

Maurice Whitten reported some progress on the work of the committee on revising the syllabus. Sister Ernestine Marie is attending a conference in Pittsburgh this week and may bring back ideas that are helpful.

The constitutional amendments recorded in the minutes of the executive committee meeting of May 13, 1955, and printed in the June issue of the NEACT *Newsletter* were approved.

Marco H. Scheer presented honorary membership certificates to Dorothy W. Gifford and Ina M. Granara in recognition of their services to the teaching of chemistry and to the Association, as recorded in citations at the May meeting.

By a standing vote the Association expressed appreciation to the co-chairmen of the Seventeenth Conference, Roland M. Whittaker and Angela Trovato, for their excellent program and arrangements.

Marco H. Scheer announced that the executive committee had accepted the invitation of the University of New Hampshire for the Eighteenth Summer Conference during the week of August 20, 1956. Louise O. C. Swenson, English High School, Lynn, Massachusetts, has accepted the chairmanship of arrangements, and Clinton S. Johnson, Rhode Island College of Pharmacy, is chairman of the program committee.

The Association voted to send greetings and best wishes to A. J. Currier, professor emeritus at Pennsylvania State University, who was unable to attend because of an operation.

MEETINGS SCHEDULED

October 8, 1955, Phillips Exeter Academy, Exeter, New Hampshire.
December 10, 1955, Northeastern University, Boston Massachusetts (joint meeting with New England Association of Colleges and Secondary Schools).
February 11, 1956, Connecticut College, New London, Connecticut.
April 14, 1956, St. Joseph College, West Hartford, Connecticut (joint meeting with the Connecticut Valley Section of the American Chemical Society).
May 12, 1956, Natick High School, Natick, Massachusetts (Annual Meeting).
August 20–25, 1956, University of New Hampshire, Durham, New Hampshire (Eighteenth Summer Conference).

LEALLYN B. CLAPP, *Secretary*

To the Editor:

The points so clearly expressed by Professor Raymond E. Kirk in his talk before the Sixteenth Summer Conference of the NEACT (THIS JOURNAL, **32**, 335–8 (1955)) on inaccuracies of present chemical terminology in teaching, call our attention again to the semantic confusions that have unnecessarily plagued teaching. Terms formerly expressing single ideas continue to be used after research and theoretical advances have split the former single ideas into several each. As Lavoisier almost put it, the word should represent the (single) idea and the idea should represent the (single) fact. A remedy would be to (*a*) classify the ideas represented by the ambiguous formula, and (*b*) separate the ideas by distinguishing signs.

An atomic symbol, such as Na, can represent: (1) the substance in general, in any form; (2) the free element; (3) an atom of the latter; (4) the kernel of the last named; (5) the nucleus of the atom; and (6) a proportional weight, such as 23 grams or 23 pounds of the element, either free or in compound.

Analogously, NaCl can represent the substance, the common salt, or 58.47 parts by weight of the latter; it is when it is interpreted as meaning a "molecule of NaCl" that it deviates from modern beliefs and merits Kirk's criticisms. Kirk cites Cu^{++} and $Cu(H_2O)_4^{++}$ as examples of bad and good symbolism, respectively. But Cu^{++} represents the substance and its oxidation state. $Cu(H_2O)_4^{++}$ represents also our idea of the composition of the mobile particle in solution. In common practice, Cu^{++} includes $Cu(H_2O)_4^{++}$, $Cu(NH_3)_4^{++}$, and $Cu(CN)_4^{--}$, unless of course it is understood or misunderstood as being *only* Cu^{++}, *i. e.*, an atom minus two electrons. The formula of an ion can represent: (1) a single particle, bearing the charge indicated; (2) the element in the given oxidation state in its compounds or as ions; (3) a proportional weight of the ion(s); and (4) the simplest hypothetical particle representing the composition, Hg^{+} for Hg_2^{++}, for example. The molecular formula can represent the analogues of these four ideas: (1) a single

polyatomic particle; (2) the substance of the compound; (3) a proportional weight of the compound; and (4) the simplest assembly of atoms or ions having that same over-all composition.

Similarly, the equation can represent several different ideas: (1) an elementary collision or reaction involving individual particles, such as $Cl_2 + h\nu \rightarrow Cl + Cl^*$, or $HAc \rightarrow H^+ + Ac^-$; (2) a statistically significant assembly of such individual elementary reactions, as $HAc + H_2O \rightarrow H_3O^+ + Ac^-$, or $H_2 + Cl_2 \rightarrow 2HCl$, a particular set of cases of which is the equilibrium of opposed reactions, as $HAc + H_2O \rightleftarrows H_3O^+ + Ac^-$, or $Ag^+ + Cl^- \rightarrow AgCl$; (3) a macro-scale process, occurring in test tube or tank, wherein some weighable material disappears and others are formed, such as $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$. Of these three ideas, the first includes those that are thermodynamically impossible on a visible scale, such as anti-Stokes quantum reactions, and can occur on a micro scale only. The second class consists of those on the atomic or molecular level which occur to a significant degree and can have an appreciable equilibrium constant. The third class consists of industrial or laboratory processes, or those occurring in nature.

The fallacies listed by Kirk and the errors often made by students in answering questions like, "Complete and balance these equations," are due in part to failure of textbook writers to distinguish among these ideas. May I therefore suggest to all textbook authors and publishers that some code of signs be adopted to separate the connotations? As examples of the items in such a code, I offer these suggestions:

(1) Single atoms, ions, and molecules will be represented by one kind of type, such as italic or light type. Another kind, *e. g.*, boldface or Gothic, will be used for macroscopic samples of weights of substances.

(2) Formulas of ionic compounds, such as sodium chloride, will be written with a pre-subscript ± to indicate ionic binding in the crystal state and complete dissociation in solution. Examples: $_{\pm}NaCl$, $_{\pm}CaCl_2$, $_{\pm}(NH_4)_2SO_4$. Such a formula will be called just that, not "molecule"; "formula weight" will replace "molecular weight" for these compounds, and solution concentrations will be expressed as "formula ratio," "formula fraction," and "formal" instead of "mol ratio," "mol fraction," and "molar." Formulas without pre-subscript will represent covalent molecules or nonpolar substances.

(3) Oxidation states will be represented by simple symbols with superscript Arabic numerals preceded by sign, such as Sb^{+5} or Cu^{+2}.

(4) Actual charges will be shown by rows of + or − as superscripts on the formulas we believe to represent the actual composition of the ionic species, such as $Cu(H_2O)_4^{++}$ or $Al(OH)_6^{---}$

(5) A single arrow will represent a change on the microscopic scale, whether or not statisically significant. A single collision or elementary change, involving one or a very few particles, can be represented by an arrow in light type; a boldface arrow will indicate a thermodynamically possible or probable reaction. Equilibrium will be represented by reversed arrows, $\rightleftarrows$, in boldface; the upper arrow will show the more favored direction.

(6) Equations for stoichiometric purposes and those representing industrial, laboratory, or visible natural processes will use equality signs, it being understood that change is from left to right, or by a combined equality sign and arrow, $\Longrightarrow$.

(7) Solids will be underlined and gases will be shown by upward arrows to distinguish them from covalent solutes. A downward arrow will indicate precipitation.

The flaws in the above suggestions should incite some author or publisher to device a good code of conventions that, even if followed only in elementary textbooks, will enable the student to distinguish among connotations and will save us from unwillingly misrepresenting nature. As examples of use of the code here suggested, we have:

$_{\pm}\underline{AgCl} \rightarrow Ag^+ + Cl^-$	A single cation and a single anion leaving an ionic crystal.
$Ag^+ + Cl^- \rightarrow {}_{\pm}\underline{AgCl}$	Deposition of a single cation and a single anion on an ionic crystal.
$Ag^+ + Cl^- \rightarrow {}_{\pm}\underline{AgCl}$	Deposition of many cations and anions in equal numbers on the ionic solid.
$Ag^+ + Cl^- \rightleftarrows {}_{\pm}\underline{AgCl}$	Equilibrium between ionic solid and solution.
$_{\pm}AgNO_3 + {}_{\pm}NaCl = {}_{\pm}AgCl\downarrow + {}_{\pm}NaNO_3$	Reaction of a given weight of silver nitrate with the chemically equivalent weight of sodium chloride, forming solid silver chloride and leaving sodium nitrate in solution.
$Fe^{++} \rightarrow Fe^{+++} + e$	Loss of an electron by a single ferrous ion, unsolvated.
$2Fe^{+2} + Cl_2 \rightarrow 2Fe^{+3} + 2Cl^-$	Oxidation of ferrous compound to ferric compound.
$2Fe(H_2O)_6^{++} + Cl_2 \rightarrow 2Fe(H_2O)_6^{+++} + 2Cl^-$	Oxidation of ferrous ion in aqueous solution to ferric ion, both hydrated.

SAMUEL WEINER

UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

To the Editor:

In my article which appeared on page 309 of the June, 1955, issue of THIS JOURNAL, I presented a classification of sources to be used for data searches in chemical libraries.

Item (*g*) of Group 1, "Publications of API Project 44," should appear instead, as part of item (*h*) in Group 3. Item (*h*) would then read: "AMERICAN PETROLEUM INSTITUTE, Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds (Carnegie Press), and other publications of API Project 44."

In my comments on Group 2, of the several sources cited, it should be noted that Gmelin alone endeavors to make a critical selection of the better sources of data.

R. E. MAIZELL

OLIN MATHIESON CHEMICAL CORPORATION
NIAGARA FALLS, NEW YORK

Film Reviews

CHEMISTRY OF COMBUSTION

Description: **16 mm., sound, 10 min.**
Producer: **Institutional Cinema Service, Inc.**
Reviewer: **R. T. Schenck, New York University**

Possible Utility: (1) *Classroom.* Not recommended.
Film Content: "Steel, (nails, file, tongs) burned in oxy-gas flame. Temperature is greatly increased, confining combustion to a small volume." Numerous examples, good and poor, of spontaneous combustion are demonstrated. "Combustion of HgSCN forms 'Snakes' (Pharaoh's serpents)."
General Criticism and Rating: "Poor Just a collection of lecture demonstrations, not too coherent or well organized, neither explained nor explaining anything. No particular connection with the title. Factually imperfect: The dehydration of sugar with concentrated sulfuric acid is *not* combustion, nor is Na amalgam the result of Hg plus NaOH. For that matter, nothing about NI_3 is combustion either. And where the 'chemistry' comes in is not apparent."

CHARACTERISTICS OF LIQUIDS

Description: **16 mm., sound, 10 min.**
Producer: **Brandon Films, Inc.**
Reviewer: **Alan W. Searcy, Purdue University**

Possible Utility: (1) *Classroom.* "I cannot recommend it as an aid in teaching college freshmen or high-school students." (2) *Other.* "This film is a very interesting one to watch and is sure to hold a student audience's attention."
Film Content: "The narrator states. . .that its purpose is to illustrate two properties of liquids—'surface films' and viscosity—and to discuss three forms of liquids—drops, jets, and bubbles.
"The properties of 'surface films' are explained with a schematic drawing of a beaker full of stationary, but pulsating molecules. The narrator states that the molecules in the bulk of the liquid are attracted by forces of cohesion in all directions, but that the molecules at the surface are attracted only in the direction of the liquid by cohesive forces. The next four scenes illustrate the ability of surface films to support a needle, wire, larvae, and pupae at the surface of a liquid.
"Three additional scenes illustrate the changes in surface tension of water when soap or chloroform is added or when heating takes place. This section of the film is concluded by a demonstration that the film of a soap solution supported on a wire hoop is strong enough to support a small wire basket.
"The brief section that follows illustrates the effect of a viscous liquid supported on a wire produced by plucking the wire, heating it, or holding it near a vibrating tuning fork. The narrator describes what is observed to happen in terms of viscosity.
"The section on drops begins with a view of drops falling into water and then of drops forming and falling. The narrator says that as drops form, surface tension opposes the force of gravity. A caption explains that a sphere has minimum surface for a given volume of liquid, and that spheres form because of surface tension. Drops of water are then shown to break into smaller drops upon striking a wax surface obliquely. It is then illustrated that bigger drops of water form under the surface of an immiscible liquid than can be formed in air, and that in a sufficiently dense medium the drops rise. A bubble of oil rotated below the surface of a salt solution is shown to throw off smaller oil bubbles. The narrator tells us that this occurs when the centrifugal force overcomes the force of surface tension.
"Jets are shown to pass each other without joining into a single jet when they are shot against each other at an acute angle. The approach of a charge of static electricity is shown to cause the jets to coalesce.
"In the section on bubbles, the formation of a tall column of soap bubbles when H_2 is pumped into a soap solution is said by the narrator to illustrate adhesion. The tendency of bubbles to pack as hexagons and the resistance of bubbles to penetration by another bubble are illustrated. Bubbles are bounced together and a smoke-filled bubble is formed inside an ordinary bubble.
"The film concludes with a brief statement that the familiar laws of cohesion and adhesion manifest themselves in the liquid state."
General Criticism and Rating: "Though the demonstrations are entertaining and often ingenious, they are not presented in a way that will add much to the student's understanding of the scientific principles that underlie the phenomena demonstrated.
"There are too many demonstrations for so short a film. On the average each demonstration lasts about 30 seconds.
"The interpretations of the demonstrations are superficial and frequently are misleading or even incorrect."
Suggestions for Improvement: "If the demonstrations were explained more clearly than they are now, they might be integrated into a useful film designed to illustrate the nature of surface tension and of cohesive and adhesive forces."

CHARACTERISTICS OF SOLIDS

Description: **16 mm., sound, 10 min.**
Producer: **American Film Registry**
Reviewer: **R. T. Schenck, New York University**

Possible Utility: (1) *Classroom.* "Might be suitable for engineering students at a very low level, but it contains absolutely nothing pertaining to chemistry."
Film Content: "This film is mistitled; it should be called 'Strength of Materials' or something of the sort. The first 40 seconds shows some quite adequate representations of Bohr models of simple atoms. The following 9-plus minutes is simply a series of shots in an engineering laboratory of tests to failure, in hydraulic presses and the like, of samples of wood, concrete, stone, and metals in compression and tension."
General Criticism and Rating: "The film as a whole, of course, can not be recommended on the basis of the 10 per cent which is of interest to chemists. The title should be deleted from the A. C. S. list at the first opportunity."

PROPERTIES OF WATER

Description: **16 mm., sound, 11 min.**
Producer: **Coronet Instructional Films**
Reviewers: **Frederic C. Schmidt, Indiana University**
Charles S. Rohrer, Indiana University

Possible Utility: (1) *Classroom.* "Can be used when teaching the physical chemistry of solutions as well as in teaching the physical properties of liquids. We here wait until the instructor has discussed both liquids and solutions before showing it."
Film Content: "This film demonstrates all of the physical properties of water, with the exceptions of viscosity and surface tension . . . . The film really is not restricted to the teaching of the physical properties of water, but to all liquids. It is particularly good on the idea of solutions, showing saturation and supersaturation . . . ."
General Criticism and Rating: "The film does an excellent job . . . . The experiments shown are well done and the explanation of the phenomena explicit . . . . This film . . . is accurate."

● CHEMICAL EFFECTS OF ELECTRICITY

Description: 16 mm., silent, 15 min.
Producer: Encyclopedia Britannica
Reviewer: Virginia Bartow, University of Illinois

Possible Utility: (1) *Classroom.* "The film has been used at the University of Illinois for the students who are taking elementary chemistry as a requirement in engineering. Careful annotation has been considered necessary. For secondary schools, a newer film would be much better."

Film Content: "This film depicts the following: representation of Volta with his 'crown of glasses' from which he produces an electric spark; boy with a 'B' battery and old-fashioned radio; production of the 'B' battery; production of a lead storage battery; demonstration of the electrolysis of water; production of a storage battery by electrolysis; electroplating; electrotyping; electroplating bath; electrolytic operations used in refining blister copper and production of aluminum; production of aluminum wire and its use in transmission lines."

General Criticism and Rating: "The film is accompanied by an explanatory pamphlet dated 1930. The subtitles are very few and commentary is needed. Several points in the printed material are out of date. Only protons and electrons are indicated in the structure of an atom. The animated diagram of the electrolysis of water shows the discharge of two hydrogen ions but does not indicate the formation of hydrogen molecules clearly. The oxygen is formed by the discharge of the sulfate ion which then removes the hydrogen from a water molecule, which leaves the oxygen. The electrolysis of brine would be a simpler, more easily explained electrolytic reaction. Some of the background such as the ancient radio, old equipment, and poor lighting detracts from the film. The production of aluminum is described as if it were made from bauxite solution."

● BAKELITE PLASTICS. FILM I

Description: 16 mm., sound, 30 min.
Producer: Bakelite Corporation
Reviewers: J. G. Walsh, Fordham University
M. J. McGuinness, Jr., Fordham University
N. H. Cantwell, Fordham University

Possible Utility: (1) *Classroom.* "Too highly specialized for ordinary chemistry students and can only be of real value to certain types of specialized chemical engineering students." (2) *Other.* "Of interest to members of the plastic industry."

Film Content: "Describes the selection of the proper thermosetting plastic mold material. It takes up in turn the various physical tests which a good plastic must undergo and describes each in detail, *viz.*, tensile strength, impact strength, dielectric properties, and shock resistance. A comparison of various types of phenolic plastic as to application is then taken up. The phenolic plastics are divided into six general classifications according to their uses: (1) shock-resistant phenolics, (2) general-purpose phenolics, (3) heat-resistant phenolics (various types of filler which are added to the first three types are discussed), (4) chemical-resistant phenolics, (5) electrical-resistant phenolics, and (6) low-loss insulation phenolics (no description of the method of attaining the last three is given). Included in the film is a great deal of advertising and description of Bakelite products."

General Criticism and Rating: "The content of the film seems to be on the whole generally accurate, especially with regard to the general physical properties of the phenolic plastics .... There is ... a great deal of repetition of operations carried out in finishing plastics and absolutely no chemical discussion of the composition of the plastic material. There is also too much advertising. The purpose of the film, namely, to act as a guide for engineers in selecting Bakelite products is adequately carried out."

Suggestions for Improvement: "The film could be greatly improved if a detailed exposition of the chemical composition of the phenolic plastics were included."

● CHEMISTRY OF FIRE

Description: 16 mm., sound, 50 min.
Producer: U. S. Navy
Reviewers: Frederic C. Schmidt, Indiana University
Charles S. Rohrer, Indiana University

Possible Utility: (1) *Classroom.* "This film has its place in a terminal course in chemistry where the idea of the course is to make the students realize that they are living in an age which depends decidedly upon chemical phenomena." (2) *Other.* "The film is all right as a safety teacher."

Film Content: "This film is particularly important as far as damage control on board ship is concerned ...". The film has about 20 minutes of the chemistry of fire, showing that solids and liquids must be first converted to a gas before they will burn. The film goes on to explain this phenomenon through experiments on flash-point and fire-point. They use one trick to show the relative amounts of vapors over oil, ether, gasoline, etc., which is quite startling—a 'shadow graph.' "

General Criticism and Rating: "The first 20 minutes of it is good on the subject of fire and oxidation in general.... We use the film every semester and like it. ...."

SOURCES OF TEACHING MATERIALS

USERS of classroom films may be glad to discover that the May, 1955, issue of the *Educational Research Bulletin*, Ohio State University, Columbus, Ohio, contains a recently-compiled list of all types of source material. The contents of this information-packed pamphlet are organized under these titles and others: Catalogs and Other Sources of Films, Filmstrips, and Slides; Radio and Television; Educational Recordings; Free and Inexpensive Teaching Aids; Pamphlets; Pictures, Charts, and Maps; Other Audio-Visual Materials.

● OPERACIONES BÁSICAS DE LA INGENIERÍA QUÍMICA

George G. Brown **and Associates, University of Michigan. Manuel Marin & Cia, Barcelona, 1955. xi + 629 pp. 551 figs. 64 tables. 22 × 28 cm. $14.**

Yo VEO al joven. El joven es un estudiante. El está estudíando ingeniería química. El carga un libro grande bajo su brazo. ¿Que es el libro? Es la traducción al español de "Unit Operations" por G. G. Brown y colegas de la Universidad de Michigan.

"Unit Operations" is well known and widely used in the English-speaking countries and also in other countries where students secure a good working knowledge of English. This translation into Spanish was made by eight professors in various universities in Spain. Not only was the text translated, but all illustrations, charts, tabulated data, and problems were changed into Spanish legends and metric units. Errors in the earlier English edition were corrected.

The availability of "Operaciones Básicas" will do much to stimulate instruction in chemical engineering in the Spanish-speaking countries if proper texts and instruction can be given in the basic subjects of material and energy balance.

KENNETH A. KOBE

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AUSTIN, TEXAS

● PHYSICAL CHEMISTRY

Farrington Daniels, **Professor of Chemistry, and** ***Robert A. Alberty,*** **Associate Professor of Chemistry, University of Wisconsin. John Wiley & Sons, Inc., New York, 1955. viii + 671 pp. Many figs. and tables. 16 × 24 cm. $6.50.**

IN A certain sense this text originated in 1913, and it is to be expected that it will be considered simply as the most recent revision in the series by Getman, Daniels, and now, Alberty. But this text is more than a revision; as before, we note evidence of careful attention to detail, logical order, and a deep interest in the subject. Here the similarity ends. It is no more correct to consider this text a revision of the 1948 edition by Dr. Daniels than to consider that the works of Aquinas are merely a revision of those of St. Augustine.

It is not feasible to cite a complete list of all the changes in the text; a definitive catalogue would defeat the purposes of a review. But we can most easily understand why this is more than a revision by comparison with the 1948 text.

The order of presentation will be familiar to old friends of the series; there are no significant modifications. The gas laws are introduced in the first few pages and the student is then carefully led to an understanding of $\Delta F = \Delta F^\circ + RT \ln Q$. The remaining chapters, one-half of the text, apply this equation to practical and theoretical cases and discuss the special branches: Conductance, Ionic Equilibrium, Colloids, Quantum Theory, Nuclear Chemistry, and, of course, Kinetics and Photochemistry. The appendix is considerably smaller; some of the material has been incorporated into the text, and information of lesser importance discarded.

The chapter on Atomic and Molecular Forces has disappeared and the material has been incorporated, in briefer form, here and there in the text. A few other sections have been transposed. For example, solid-gaseous equilibria have been moved to their earlier position—in the same chapter with the phase rule. Some chapter titles have been changed to indicate their contents more accurately.

Throughout the text there are many detailed changes, this is the outstanding feature. Almost every paragraph retained from the 1948 text has been revised. Many new paragraphs have been substituted and others have been added. In each instance, the matter discussed is clearer than before. This is indeed a text written for the student. To site four examples from many: Miller indices are no longer an enigma; the student should have no trouble in understanding why salt lowers the freezing point of water; Morse curves are used to help the student understand photoexcitation; here and there a few exercises in the derivation of relations are interspersed.

New and better illustrations have been prepared; only a few old ones remain. The tables and many of the graphs are now easier to read. The interesting historical allusions have been retained. Several recent references to THIS JOURNAL and to others have been added.

The material is up to date; in so far as they are appropriate to an elementary treatment, the advances of the past seven years have been included. A few of these are: the determination of molecular weight by the scattering of light, microwave spectroscopy, the kinetics of enzyme catalysis, a (far too brief) discussion of radiation chemistry, and C^{14} dating.

Many of the problems are new, and as before, they are arranged in graded sets with answers supplied for the first set only. Although only actual use will tell, it seems possible that the students will be less successful than before in their attempts to solve the problems by comparing them with examples in the text and applying the example to the problem without thought.

The new sketches, in a psuedo three-dimensional style, and the changed graphs, one ordinate and abcissa, with short scale markers to indicate distances from the origin, constitute a decided improvement. It is suggested that the few remaining old style sketches and graphs be altered in the next edition, or possibly in the next printing.

JAY A. YOUNG

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● QUANTITATIVE ANALYSIS

Albert Frederick Daggett, **Professor of Chemistry, University of New Hampshire, and** ***William Buell Meldrum,*** **Professor of Chemistry, Haverford College. D. C. Heath and Company, Boston, 1955. x + 470 pp. Figs. and tables. 16 × 24 cm. $5.**

THIS text is divided into two parts; one part contains a general discussion of principles and techniques and the other includes laboratory procedures. The analytical determinations are the common, classical ones that have been successfully carried out by students of quantitative analysis for years. They include the common volumetric and gravimetric methods for simple systems, limestone, and brass. The part on principles and techniques was written with the feeling that students entering the sophomore course in elementary quantitiative analysis have not had sufficient training in some of the basic concepts of chemistry. For this reason the authors include chapters on topics such as ionic theory and quantitative ionic equilibria.

The text is devoted almost exclusively to an elementary discussion of gravimetric and volumetric methods of analysis. The volumetric methods include acid-base titrations, oxidation-reduction titrations, and precipitation titrations. The authors chose to omit discussions of instrumental methods of analysis with the exception of electrolytic and conductometric methods. Of these two methods, only the electrolytic is covered in a laboratory procedure, *i. e.*, the determination of copper in brass.

In general, the presentation of theory is concise and lucid. The order of arrangement of chapters may be open to question. For example, the treatment of data immediately follows the introductory chapter of the book; thus, experimental data and terms are introduced which are totally foreign to the student. The instructor may wish to postpone this chapter until later.

The reviewer found only a few inconsequential errors of type and fact. However, there are some cases in which the authors could be more complete or correct. One of these is the definition of the term *solution*, on page 58. Another example is the nomenclature of compounds. Adherence to the recommendations of the Committee of the International Union of Chemistry would eliminate such names as bioxalate and bichromate and would improve such names as auricyanide, platinicyanide, and ferrithiocyanate.

At the end of each chapter of theory there are a number of problems with answers. A considerable number of the problems are not well chosen to illustrate the theory which has been covered. Students would profit by solutions to more problems illustrating theory. If the solutions to the problems in the text were always set apart from the body of the printed material they would be more effective as teaching aids.

The authors give a concise yet readable presentation of the elements of quantitative analysis, which would find use in a one-semester course. In the opinion of the reviewer, the text is too limited for use in a full-year course in elementary quantitative analysis. Many important topics have been omitted or treated in a very limited fashion. Examples are buffers, analytical separations, overvoltage, and the effect of complex ions and hydrogen ions on oxidation potentials. The text does not discuss more recent analytical techniques; it lacks the touch of modern trends in analytical chemistry.

GLENN H. BROWN

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• THE IDENTIFICATION OF ORGANIC COMPOUNDS

Stig Veibel, **Professor of Organic Chemistry, University of Technology, Copenhagen. Fourth edition (first English edition). G. E. C. Gad, Publisher, Copenhagen, 1954. xv + 346 pp. 15 × 21.5 cm.**

VEIBEL'S book is a manual of qualitative and quantitative methods of identifying organic compounds which has been sifted from experience in teaching such a course since 1927. As in other European texts, in general, in comparison with current American texts, less direct assistance is given the student. For example, no systematic solubility scheme is given in so many words though a student might devise one from the discussion given on solubility of organic substances.

Much of the emphasis on identification of functional groups is by color reactions, many of which are new and others of which have been published in Scandinavian journals not always accessible here. Some of the tests are quite new since many of the publication dates of references are in the 1950's. American chemists will want to try these new tests for comparison with known methods. For example, Veibel suggests the use of the diazonium salt of sulfanilic acid as a color test for alcohols. This has not been published elsewhere (at least Veibel gives no reference). Veibel also includes some old methods which have not been popular here, for example, the Victor Meyer nitrolic acid tests for alcohols.

Both qualitative and quantitative methods are given for 23 functional groups into which organic compounds are divided.

Veibel himself has been active in research on quantitative estimation of functional groups. One of his contributions is to convert a functional group into a substance which can be titrated as an acid or base. For example, *p*-carboxyphenylhydrazine is used as a reagent for carbonyls and the product is then titrated as a carboxylic acid. He has applied this type of reaction to a number of other cases.

There are a few illustrations of quantitative apparatus taken from recent publications. At the end of the book are four pages on concentration of reagent solutions, a five-page author index of references cited, and an eight-page subject index.

The text may not make inroads into the sale of American books on this subject, but teachers will want to try many of Veibel's suggestions.

LEALLYN B. CLAPP

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• A COMPANION TO PHYSICAL AND INORGANIC CHEMISTRY

R. W. Stott, **formerly Senior Science Master, Rugby School. Longmans, Green and Co., New York, 1955. ix + 184 pp. Figs. and tables. 13 × 19 cm. $1.75.**

THIS book is designed to help an English secondary-school student prepare for university scholarship exams. It may well be that each teacher of beginning chemistry in this country should have a copy at hand to aid him in setting standards for his students. This reviewer would guess, however, that the teacher's sense of frustration would rise faster than the standards of his course, though it might well spur on the better students.

The dozen or so errors of fact—water molecules exist in groups, hydrogen bonds are more than electrostatic, electrode potentials are due only to solution potentials, over-simplification of group valencies, a single chloride bridge in Al_2Cl_6, two valence electrons in chromium, etc.—are unfortunate but not overwhelming.

American students might well read this book, but mainly in perspective. Their own education is usually such that this approach seldom fits.

J. A. CAMPBELL

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• METALLURGY OF THE RARER METALS. NUMBER 3: MANGANESE

A. H. Sully. **Academic Press, Inc., New York, 1955. xiv + 305 pp. 138 figs. 55 tables. 14 × 22 cm. $6.50**

THIS third volume in a new series that was begun last year maintains the high standards of the previous two volumes (THIS JOURNAL, 31, 670 (1954)). Even though manganese is used in large tonnages, it is not a familiar element to most chemists or metallurgists, particularly as the pure metal. This up-to-date treatise reviews the occurrence and ores; the production of ferro-manganese alloys and of commercially pure manganese; methods of conserving manganese; physical properties of manganese; constitution and properties of binary and ternary alloys; and electro-depositing of manganese coatings and surface reactions at high temperatures. The chemistry of manganese is confined mostly to reactions that are used in its reduction from the various ores, whereas, as is appropriate in a book on metallurgy, more than 100 pages are devoted to all the known alloy systems.

In recognition of the growing realization that manganese is used wastefully in the iron and steel industry, considerable attention is given to the role it plays in steel making. As yet, however, no deoxidation procedure has been worked out that

also reduces the sulfur content of steel so effectively as does addition of manganese. More than 14 pounds are used to produce one ton of steel, and most of this added manganese ends up in the slag. Procedures to recover it are now being intensively evaluated. This is of particular importance to the United States which in 1952 produced only 106,000 metric tons, but imported 2,140,000 metric tons from India, Africa, Central and South America, Turkey, the Philippines, and Indonesia.

Electroplating with manganese is not a familiar art, even though electrowinning of manganese is common practice. Bright coatings can be electrodeposited from aqueous solutions onto steel, aluminum, copper, and zinc. While such coatings impart corrosion resistance because of rapid oxidation at room temperature, they soon become covered with an unattractive, dark brown film.

Manganese at room temperature is hard and brittle and cannot be worked readily. Alloys of electrolytic manganese with copper, on the other hand, can be worked hot and then quenched without damage. Similar copper alloys with additions of nickel, still maintaining very high manganese contents, can be forged and rolled. Such alloys have not as yet found commercial applications.

Each chapter is provided with a very complete bibliography. There are both a table of contents and an index. The latter seems skimpy in that the alloys listed in the table of contents are not repeated individually in the index. Also, the word "alloys" is misplaced under manganese. It is surprising to find in a book published ten years after the close of the Manhattan Project a reference on page 121 to the nonexistant element, "masurium." There is nearly as much known about technetium (atomic number 43) as about manganese!

The aim of the series, "to provide a readable work of reference on the background and the metallurgical, chemical and physical data" of several rarer metals, is being competently realized. These books will find acceptance in every technical library.

LAURENCE S. FOSTER

BELMONT, MASSACHUSETTS

● DEGRADATION OF VINYL POLYMERS

H. H. G. Jellinek, **Senior Lecturer in Physical and Inorganic Chemistry, University of Adelaide, South Australia. Academic Press, Inc., New York, 1955. x + 329 pp. 123 figs. 51 tables. 15.5 × 23.5 cm. $8.50.**

THE forming of vinyl polymers from simple molecules is a more dramatic occupation than the reverse procedure of breaking down these fabulously useful materials. However, the degradation of polymer molecules is an important problem, having both theoretical and practical interest for the chemist, physicist, and engineer. From the theoretical point of view, an understanding of degradation kinetics and mechanism improves our knowledge of the basic nature of the original polymer. It is of practical importance to know the limitations of various polymers in environments in which their use may be contemplated, or perhaps how to alter the properties of certain polymers in a desirable way by applying to them the influences which can cause controlled degradation. Further, the recovery of monomer by thermal cracking of scrap polymer is said to be of economic importance in certain cases.

"Degradation of Vinyl Polymers" begins with a review of the formal mathematical theories of degradation; this serves as background for the later treatment of the available data. The three principal chapters of the book then deal with degradation of polymers in bulk (*in vacuo*), in solution and under oxidative conditions, and under the application of mechanical and ultrasonic forces.

In few cases is there a completely developed picture of the degradation, and the author frequently gives clear statements of what remains to be done, along with suggested methods of attack on the problem. It is apparent that experimental work in this field must be designed with unusual care to yield data capable of significant interpretation. Helpful advice is given by the author for those who would undertake work of this kind.

Historical background is well developed, and the author is discriminating in his selection of the most pertinent references for discussion in those areas where the literature is vast. Diagrams of apparatus and graphical presentation of data add greatly to the relative ease, profit, and pleasure with which this book can be read. This reviewer was particularly pleased with the treatment of the question recently posed as to whether polymerization and degradation may, in certain cases at least, be facets of a single equilibrium process.

Typographical errors, though frequent, are not troublesome.

ELLINGTON M. BEAVERS

ROHM & HAAS COMPANY
PHILADELPHIA, PENNSYLVANIA

● MODERN PHYSICS FOR THE ENGINEER

Edited by *Louis N. Ridenour,* Vice-president, International Telemeter Corporation. McGraw-Hill Book Co., Inc., New York, 1954. xix + 499 pp. Many figs. 16 × 23.5 cm. $7.50.

IT WILL be unfortunate if chemists are inclined to pass this volume by because of its title. It was chosen by the editor on the assumption that today's physics is tomorrow's engineering. Many chemical educators who have been looking for authoritative reviews of theoretical topics in the areas of physics most closely related to the subject matter of conventional chemistry courses will be rewarded by the discovery of this volume. The section under the title The Laws of Nature includes particularly interesting chapters on the solid state (Seitz), nuclear structure (Fowler), and elementary particles (Panofsky). The second section, headed Man's Physical Environment, includes easy-reading chapters on astrophysics (Greenstein), geophysics (Griggs) and oceanography (Revelle). The chapter on semiconductor electronics (Bardeen) from the third portion of the volume, entitled Information and its Communication, will also be a fortunate discovery for those wanting a short, accurate survey of this important subject that even has captured the fancy of the popular press.

Each of the 18 chapters carries a limited bibliography. The volume as a whole is adequately indexed. It is well illustrated with pertinent plates and diagrams, but relatively few tables of data.

WILLIAM F. KIEFFER

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WOOSTER, OHIO

● DIELECTRIC BEHAVIOR AND STRUCTURE

Charles Phelps Smyth, **Professor of Chemistry, Princeton University. McGraw-Hill Book Co., Inc., New York, 1955. x + 441 pp. Figs. and tables. 17 × 24 cm. $9.**

THERE is a substantial modern literature on dielectrics, but most of it is written by physicists for physicists. For about 25 years, chemists have depended on Debye's classical Baker lectures (1929) and on Smyth's American Chemical Society monograph (1931), supplemented by occasional review papers. The new volume will therefore be universally welcomed by chemists, because it presents an up-to-date survey of the correlation between electrical properties and molecular structure, written by one of the foremost research chemists in the field, who simultaneously is a master of exposition.

The book begins with two chapters on fundamental theory. It is naturally a matter of personal preference; this reviewer feels that it would have been sounder pedagogy to begin with the Onsager theory and then show that the Clausius-Mosotti equation is a special limiting case of the more general theory, rather than to present the material in its chronological historical sequence.

The theoretical introduction is followed by three chapters on experimental results and their interpretation, for gases, liquids, and solids. This section includes recent work on solutions of electrolytes, radar-range dispersion, ferroelectrics, electrets, and polymers—all subjects which have been opened to research since 1930. Chapter VI is a compact review of measuring methods and includes an excellent bibliography. Chapter VII is a practical account of what to do with data once the measurements have been made. Chapters VIII to XIII (pp. 228–402) contain a systematic treatment of the relationships between dipole moments and molecular structure for typical examples of all the chemical compounds which have ever been investigated. The book closes with a useful chapter on electronic and atomic polarization.

It is a pleasure to recommend this treatise enthusiastically to organic and physical chemists, from research workers to graduate students. Even physicists will undoubtedly find it a useful source of information.

RAYMOND M. FUOSS

YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

• AN ADVANCED TREATISE ON PHYSICAL CHEMISTRY. VOLUME 5: MOLECULAR SPECTRA AND STRUCTURE. DIELECTRICS AND DIPOLE MOMENTS

J. R. Partington, Emeritus Professor of Chemistry, University of London. Longmans, Green and Co., New York, 1954. x + 565 pp. Many figs. and tables. 16 × 25.5 cm. $15.50.

THIS volume continues the well known series. The first 286 pages are on molecular spectra, continuing the subject of the preceding volume on physicochemical optics. Most of the other 279 pages are on the properties of dielectrics. There are 77 pages on the measurement of dielectric constants, 177 pages on dipole moments, and 12 pages on hyperelectrics. The index has 13 pages.

This series is generally comprehensive rather than critical. In the present volume, however, the author notes that some of the sections on molecular spectra are based on lectures given over a period of years, and that he has firsthand knowledge of certain subjects in the latter part of the volume. A more unified and critical treatment and a more selective citation of references make these sections more valuable than most in this series.

This volume refers freely to previous ones in the series. Although such references prevent this volume from standing by itself, it is easier to read, for the discussion is not encumbered with details of physics and chemistry that many readers will not need. Mathematics, however, is discussed at the place where it is first used. In this volume, there are rather extended parenthetical sections on the integrals and functions associated with the wave equation, on matrix transformations, and on group theory.

The treatment leads up to, but does not usually include, the topics of current research interest. Even when current topics are included, the viewpoint is that of years or decades ago, with more recent ideas presented as modifications.

There are many loose statements and minor errors in some sections. For example, on page 34, "The average restoring force $\frac{1}{2}kx$ may be regarded as measuring the strength of the bond. Some values calculated are: ...." The table following gives the wave number for the bond and k, but not $\frac{1}{2}kx$. Also, the units of k are given in the table as dynes, which would be correct for $\frac{1}{2}kx$ and those of $\frac{1}{2}ka$ (a is the maximum value of x) further on in the text as ergs. (Units are treated carelessly throughout. The volt is used interchangeably, without apology or explanation, as a unit either of energy or of potential, as has been the practice in laboratory jargon. Wave number and frequency are distinguished in the symbols, but not always in the text.) On page 35, r in the first equation is not the r of the referenced figure, whereas r in the next line of the same equation is.

Symbols and terminology are not consistent throughout the book, but apparently depend on the usage of the authors cited. For example, the dielectric constant is represented by K in an equation on page 39 with a reference to a later section (page 368) in which the same equation is discussed in detail, but using ϵ instead. There is no list of symbols. The omission is defended by the following statement: "...since the symbols are those used by specialists, a list of symbols would serve no useful purpose, the same symbols being used with different meanings by actual workers in the different fields." Such defects as these are not serious and will not delay a mature reader, but they are liable to delay a student.

This book, like others of the series, seems most useful to those who seek a comprehensive presentation of physical chemistry from which they can make their own selection. It should also be useful to students who are already acquainted with the subject and who wish to explore its background further.

CARSTEN STEFFENS

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STANFORD, CALIFORNIA

• EXPERIMENTS IN ORGANIC CHEMISTRY

Louis F. Fieser, Sheldon Emery Professor of Organic Chemistry, Harvard University. Third edition. D. C. Heath and Company, Boston, 1955. xii + 368 pp. Many figs. and tables. 18 × 23.5 cm. $5.25.

FROM inside the front cover which in bold type tells you what to do "in case of accidents," to inside the back cover which contains tables of atomic weights, acid and base constants, and data on buffer solutions, this laboratory text is "top-notch." Previous editions have enjoyed wide popularity among academic organic chemists. In the opinion of the reviewer the third edition will be even more widely popular. The text is profusely illustrated with photographs, line drawings, and graphs. Sixteen color photographs showing various pieces of apparatus and various operations are included in the first eight pages following the table of contents. Most of these are reproduced in black and white at the appropriate point in the text. There are also numerous plates showing ultraviolet and infrared absorption spectra of various compounds.

The format of the text is, in the opinion of the reviewer, the best of any similar book on the market and is far superior to the previous edition. The type is relatively large and bold with adequate spacing to facilitate reading. The margins are two inches wide. Section headings and succinct notes are shown in bold-face type in the margins. The paper is of a good quality and the binding is very good. Dr. Fieser suggests that the attractive cover can be preserved if treated with three coats of clear plastic lacquer.

This edition maintains the high standards set by previous editions with regard to the experiments included and the discussion of special laboratory techniques. A section on use of the literature discusses recently published references such as "Elsevier's Encyclopedia of Organic Chemistry" and Velluz's "Substances Naturelles de Synthise." There are also sections on solvents and reagents, of which the section on reagents deserves special commendation. The 320 reagents included are arranged alphabetically and are also indexed according to type—*e. g.*, alkylating agents, complexing agents, etc. The list necessarily could not be complete but does contain many reagents which have found application in only one specialized field. The citation usually includes the molecular weight, physical constants, name of supplier or reference to a method of preparation when the reagent is not commercially available, and leading references to literature pertaining to reactions and uses of the reagent. There are many literature references, more than 200 as recent as 1953.

Not all experiments in the previous edition have been retained. Those which have been retained have been extensively revised. Several meritorious modifications are: many semimacro or semimicro experiments; more synthetic reactions sequences with alternative routes and procedures, which permits the student to

use more initative; more unknowns and experimental problems. New experiments included in this edition include those on elution and paper-strip chromatography, enzymatic and spontaneous resolution, formation of geometrical isomers, and cost calculations.

In this reviewer's opinion, the text will serve admirably for the undergraduate organic chemistry laboratory. It may be used also as a constant source of help for graduate students in research.

The Instructor's Manual (23 pp., available for 40¢) will prove especially helpful in planning organic laboratory work as it has a rather complete list of chemicals needed, suppliers, and up-to-date prices. Also included are many helpful suggestions with regard to the experiments included in the text.

WILLIAM B. COOK

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WACO, TEXAS

● CHEMISTRY OF THE PESTICIDES

Donald E. H. Frear, **Professor of Agricultural and Biological Chemistry, Pennsylvania State University. Third edition. D. Van Nostrand Co., Inc., New York, 1955. vi + 469 pp. 32 figs. 19 tables. 16 × 23 cm. $8.**

THE first edition of this well known and valuable text and reference book appeared in 1942, with 300 pages; the second edition was published in 1948, with 417 pages; this third edition has 469 pages despite the deletion of detailed analytical procedures for insecticides and fungicides (which occupied 68 pages in the first edition and 73 pages in the second edition). This necessary increase in pagination reflects very well the growth and recognition accorded this field of endeavor.

In general, this third edition represents an extensive revision of the second edition, with the inclusion of many new insecticides, fungicides, herbicides, and, for the first time, rodenticides of current interest. The seven parts of the book are: I, Synthetic Organic Insecticides (138 pp.); II, Natural Organic Insecticides (94 pp.); III, Inorganic Insecticides (45 pp.); IV, Fungicides (79 pp.); V, Herbicides (36 pp.); VI, Adjuvants (24 pp.); and VII, Rodenticides (15 pp.).

This book will be even more valuable than its predecessors as an authoritative, surprisingly complete compendium of information on origin, general chemistry, properties, methods of preparation, featured applications, and some pertinent chemical reactions of the four major classes of pesticides.

As with the previous editions, Dr. Frear has written this book with skill and certainty. The index is commendably complete, and very few typographical errors are apparent. There may be some confusion among readers not familiar with organic chemistry as to which of the structural formulas containing carbocyclic rings are aromatic and which are saturated for many of the compounds represented.

"Chemistry of the Pesticides" is highly recommended for the teacher and student interested in pesticides, and for the research worker looking for a convenient and very complete catalogue of basic facts about all currently important pesticidal chemicals.

F. A. GUNTHER

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● DESIGN AND ANALYSIS OF INDUSTRIAL EXPERIMENTS

Edited by *Owen L. Davies.* Hafner Publishing Company, New York, 1954. xiii + 636 pp. 16 tables. 16 × 25 cm. $10.

THIS book, which is the joint work of George E. P. Box, Lewis R. Connor, Wilfred R. Cousins, Owen L. Davies, Francis R. Himsworth, and George P. Sillitto, marks an important milestone in the application of statistics to the physical sciences. With a single exception, noted below, the field of statistical design is extremely well covered. But the principal value of the book lies in its particularly appropriate method and plan of presentation and in its lucid style. The reader soon feels that an attempt is made to help him solve his problems, rather than to force upon him artificial problems for which statistical solutions happen to exist.

The introductory first chapter is followed by one entitled The Planning of Simple Comparative Experiments, which is an excellent, though brief, exposition of the main principles underlying the statistical method. Chapter 3, entitled Sequential Tests of Significance, while interesting and important, can be omitted in a first study of the subject. Beginning with Chapter 4, the reader is gradually led into experimental designs of increasing complexity. Randomized blocks, Latin square designs, incomplete block designs, and factorial as well as fractional factorial experiments are discussed in great detail and illustrated by means of numerical examples. In the factorial designs a clear distinction is made between qualitative and quantitative factors, and a much neglected subject, the use of regression methods in combination with analysis of variance, is adequately treated. The last chapter deals with a recent contribution to statistics, the sequential method developed by Box and his co-workers for the determination of optimum conditions, the most important application of which is the search for maximum yield conditions in chemical manufacturing processes.

This reviewer has only one major complaint in connection with this excellent book: the omission of an adequate discussion of partially balanced incomplete block designs. Indeed, experiments in the physical sciences are often characterized by relatively small random errors but large systematic errors. Therefore, a small number of replications is generally sufficient, and the presence of several levels of precision is not objectionable as long as the comparison of lowest precision is still satisfactory.

This book is highly recommended to experimental workers in the physical sciences.

JOHN MANDEL

NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C.

● BASIC LUBRICATION PRACTICE

Allen F. Brewer. **Reinhold Publishing Corp., New York, 1955. xiv + 286 pp. Many figs. and tables. 15.5 × 23.5 cm. $6.75.**

AFTER an opening chapter on how operating conditions affect lubrication and a second chapter on the significance of physical tests of lubricants, the book devotes 19 chapters to mechanical and design features of machinery and its parts for successful lubrication. Final chapters are on storage, reconditioning used oils, and nonpetroleum lubricants.

● ALUMINUM PAINT AND POWDER

Junius David Edwards **and** ***Robert I. Wray.*** **Third edition. Reinhold Publishing Corp., New York, 1955. viii + 219 pp. 76 figs. 21 tables. 15.5 × 23.5 cm. $4.50.**

How aluminum powder is made and its use in metallurgy, plastics, and other industries. Aluminum paints are of various types and have both general and specific applications to wood and metals.

● FABRICATED MATERIALS AND PARTS

Theodore C. DuMond. **Reinhold Publishing Corp., New York, 1955. v + 322 pp. 117 figs. 19 tables. 15 × 22 cm. $6.50.**

SOME production methods for producing small parts are discussed—*e. g.*, castings, forgings, extrusion, powder metal parts, spinning, electroforming, bonded, molded plastics, and formed, nonmetallic materials. Cost, production, and design factors are discussed.

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VOLUME 32, 1955

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(1) COHEN, J. B., "Organic Chemistry for Advanced Students," 5th ed., Longmans, Green and Company, New York, 1928.

References to explanatory notes such as (1) occasion on which paper was delivered, (2) acknowledgments, (3) definitions of obscure or unfamiliar terms, (4) changes in address, etc., are to be designated in the text by superior numbers in sequence with other footnotes in the article. Such a footnote should be inserted as a separate line (or lines) immediately following the word to which it refers and should be separated from the text by lines.

4. Illustrations. Not all articles lend themselves to illustration, but articles which do should be accompanied by as many pertinent illustrations as possible. The best possible selection of illustrations available will be made by the editorial staff. As a rule, apparatus, particularly if complicated, is best presented by means of line or working drawings. Photographs are sometimes sufficient, however. When both can be obtained, it is generally desirable to include both with the manuscript. Unless lettering can be done by one of the mechanical devices it should be in pencil only.

Photographs should have a gloss finish and should be at least post-card size—larger, if possible. Only prints which are unblurred and which show sharp contrast between light and dark areas can be satisfactorily reproduced. Authors should exercise scrupulous care in crediting photographs which require credit.

Line drawings should be carefully prepared in *black India ink* on plain white drawing paper, blue tracing cloth, or blue-lined coordinate paper twice or three times the size desired in the printed cut; it is convenient, when permitted by the scale required, to have them the size of the manuscript.

For *graphs* coordinate paper should be printed in *blue* only, with the important coordinate lines ruled over in black; the black-ruled square should in general not be less than ten millimeters on a side; the lines of the curves should be the heaviest, except the frame; points on the curves should be indicated by true circles, not crosses. All lines, legends, numbers, and letters which cannot be set in type at the margin of the cut but must constitute a portion of the cut itself are to be so proportioned that they will be clearly legible in the cut. The numbering of the coordinate axes, the number of the figure, and any necessary explanations of the figure should be printed in pencil in the margin of the sheet, as they are usually set up in type rather than reproduced from the drawing. Typewritten designations are not black enough to reproduce satisfactorily. Where lettering cannot be done adequately, designations left in pencil can be taken care of in the editorial office.

Tables should be inserted in the body of the manuscript at the proper place.

All photographs, line drawings, and tables should be provided with self-explanatory titles or legends. Each illustration should be marked in pencil on the margin with the name of the author and the title of the article to which it refers.

Authors are invited to examine the series of articles by E. M. Hoshall entitled "Chemical Drawing" ["I. Fundamentals of chemical drawing," J. CHEM. EDUC., 11, 21–3 (1934); "II. Conventional representation of materials and equipment," *ibid.*, 11, 23–7 (1934); "III. Arrangement of drawings," *ibid.*, 11, 154–8 (1934); "IV. Charts, graphs, and diagrams," *ibid.*, 11, 235–41 (1934); "V. Photographs," *ibid.*, 11, 546–50 (1934).].

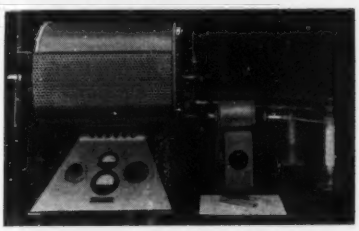
5. Reprints. A reprint price list is printed on the reverse side of the order slip which accompanies galley proofs. Special rates for reprints in 6″ × 9″ page-size may be had upon application to the *Business Manager*, Mack Printing Co., 20th and Northampton Sts., Easton, Pa.

Out of the Editor's Basket

NEW APPARATUS & EQUIPMENT

▸ Ledoux & Company, 359 Alfred Ave., Teaneck, New Jersey, announces that, after extensive testing, its new Hydrogen-Determinator is commercially available.

The increasing demand for the determination of hydrogen in metals and alloys —particularly in titanium and its alloys has resulted in a desire for faster, easier methods of laboratory analysis, of absorbing considerable hydrogen.



The new Hydrogen-Determinator—based on the combustion technique—reduces the time per determination to 20 minutes in a wide variety of metals, including titanium, zirconium, cerium, tantalum, niobium, molybdenum, tungsten, nickel, cobalt and their alloys. It determines hydrogen in concentrations as low as 0.003% and as high as those occurring in metal hydrides.

▸ A Guarded Predictability Flowmeter, designed especially to withstand the shocks of hard laboratory and industrial use, has recently been introduced by the Emil Greiner Co., 20–26 N. Moore St., New York 13, N. Y.

▸ The Electrostatic Voltmeter developed by the Institute of Textile Technology is now being manufactured by Custom Scientific Instruments, Inc., Kearny, New Jersey. The Voltmeter was designed to detect and measure electrostatic charges on textile materials during processing. Other industries other than textiles with static problems will find this instrument extremely useful. This unit is portable and may be aimed like a gun. It is extremely sensitive, with provisions made to permit reduction of sensitivity to one-tenth or one one-hundredth. The Electrostatic Voltmeter will quickly locate a charged area; give an indication of the amount of electrical charge on moving or stationary equipment or materials; and determine the polarity of the charge.

▸ The development of the new model #52LC $4^1/_2$-in. × 10-in. Laboratory Size High Speed Three Roll Mill has been recently announced by Charles Ross & Son Co., Inc., 148–156 Classon Ave., Brooklyn, New York.

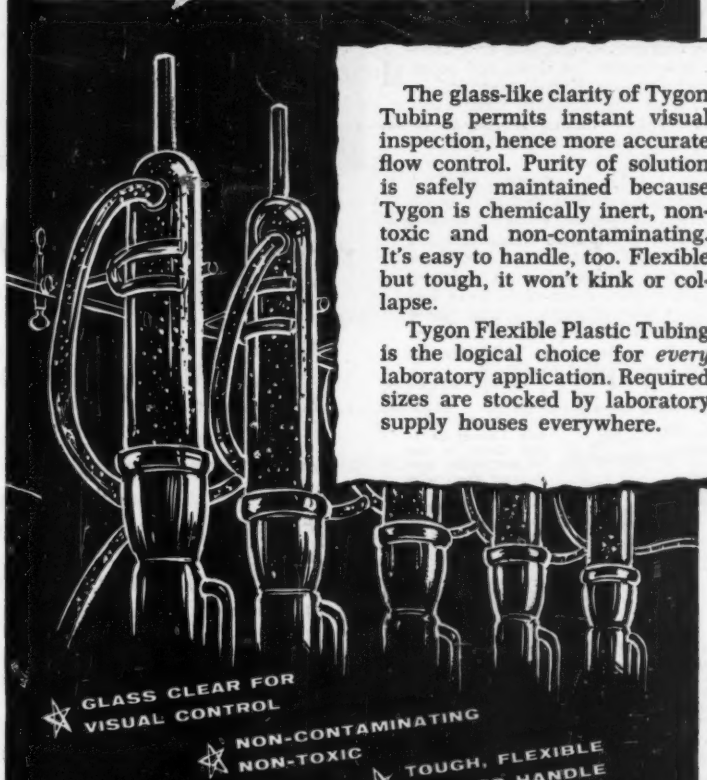
The new #52LC $4^1/_2$-in. × 10-in. Mill may be operated as a conventional Mill with fixed center roll and four-point adjustment or can be operated with floating center roll and two-point adjustment. When differences in pressure between feed and takeoff rolls are desired, the center roll is fixed position. When equalized pressures are preferred, the Mill can be converted within minutes to a self-aligning or floating center roll. To convert from one type of operation to the other can be done easily, by any operator, without the use of special tools or kits.

▸ A new automatic pipet rinser made completely from polyethylene is now available. This rinser is so designed that it will fill and drain in less than two minutes. The inlet is serrated to hold a flexible tube securely; the outlet is fitted with a standard $^3/_4$-in. pipe female ell so that a permanent drain connection is possible, or it may be fitted with a piece of flexible hose.

This rinser is designed for use with the Nalgene polyethylene pipet holder. Further information may be obtained by writing to Emanuel Goldberg, The Nalge Co., Inc., Rochester 2, New York.

▸ The new Special Purpose C.R.C. Labwasher is now available. It has been designed to solve specialized problems of washing, rinsing, and drying various types, sizes, and shapes of laboratory glassware. By the use of a simple water selector switch any cycle you need or wish to repeat is immediately available. The Special Purpose Model is a flexible machine which is adaptable to any particular requirements.

TYGON flexible plastic TUBING
...aids process control



The glass-like clarity of Tygon Tubing permits instant visual inspection, hence more accurate flow control. Purity of solution is safely maintained because Tygon is chemically inert, non-toxic and non-contaminating. It's easy to handle, too. Flexible but tough, it won't kink or collapse.

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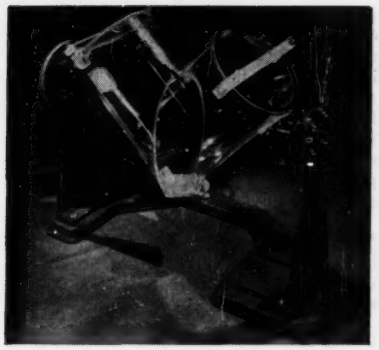
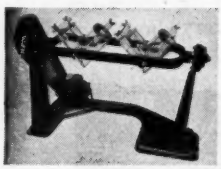


PRE-TEST Your Production Blending In The Lab

Unique design of p-k twin shell blenders allows exact scale-up of lab tests to production runs

Here's the one piece of blending equipment that has everything: a mixing action that blends most materials perfectly in 3 to 5 minutes . . . large access openings and smooth baffle-free interiors for fast and easy charging, discharging and cleaning . . . interchangeable shells and accessories that give exceptional versatility . . . *and* . . . a unique, patented design that provides identical mixing results in all sizes, from one pint lab models up to 500 cu. ft. production units.

p-k twin shell lab blenders are used for small production runs as well as research in hundreds of plants. Priced low and available from stock. Dust-tight, corrosion and abrasion-resistant Lucite shells are standard. Also available in stainless steel. Lightweight cast aluminum base has sturdy grey crackle finish, adjusts for 4 and 8 quart shells and yokes. G.E. motor is 1/20 HP, single phase, 115 volts, 60 cycle, AC. Chain guard furnished.



Yoke Model holds two 1-quart or 1-pint shells, or one of each, or one 2-quart shell with either, or adapts into a standard 4 or 8 quart blender. Handles two jobs at once.

Intensifier Bar Model gives particularly intense local mixing action, breaking up lumps, dispersing liquids into solid mixes.

Write for p-k catalog 13. The Patterson-Kelley Co., Inc., 2620 Lackawanna Avenue, East Stroudsburg, Pa.

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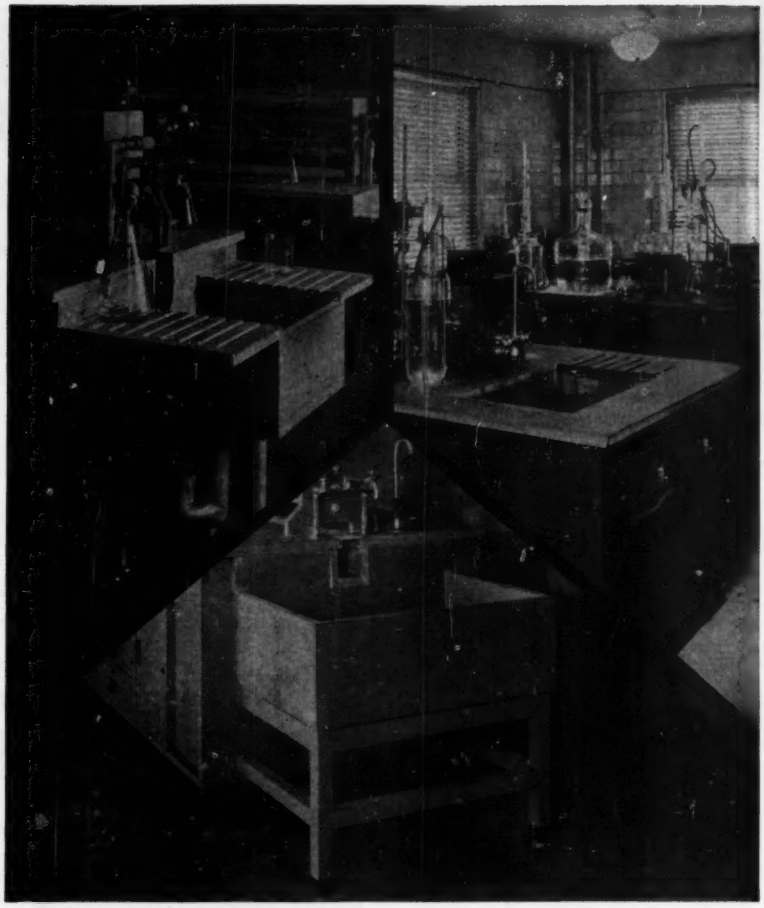
Offices: New York, Chicago, Philadelphia, Boston and other principal cities



Let's talk "SPECIAL SIZES"

The size and depth of sinks for laboratory and industrial use should be determined by the job they have to do — *and not by available standard sizes!*

With Alberene Stone sinks you can specify any size and depth — without paying a premium.

And with Alberene Stone you get — *the natural silicate stone with the surface that goes all the way thru.* Its all-silicate mineral components resist chemical attack. Low absorbency makes it essentially nonstaining. Discolorations can be removed by scouring or honing without harm to the surface.

For information and technical assistance, address: Alberene Stone Corporation, 419 Fourth Avenue, New York 16, N. Y.

ALBERENE STONE

provides LOW ABSORBENCY protection

Bulletin L-A-12 containing full details is available by writing on company letterhead to The Chemical Rubber Co., 2310 Superior Ave., Cleveland 14, Ohio.

▸ For the first time, a small, low-priced electric hygrometer humidity controller known as the Humistat, is available. The Humistat (patent pending), so-named because it is the electronic successor to mechanical humidistats, automatically operates large or small humidifiers, dehumidifiers, and air conditioners to maintain humidity control within plus/minus 1.25% relative humidity. The Humistat is said to be so sensitive that the moisture from a person's hand will operate it. Descriptive *Bulletin 2273* is available from the manufacturer, American Instrument Company, Inc., Silver Spring, Maryland.

▸ A new air dryer, originally developed for use with a precision infrared spectrophotometer, is now available from Beckman Instruments, Inc., Fullerton, California.

▸ Applicable to all open-type liquid containers and operating in any electrically conductive liquid, Blue M's new Portable Electronic Liquid Leveler automatically maintains liquid level of bath mediums within a level constancy of plus/minus 0.046 inches. It is manufactured by Blue M Electric Co., 138th & Chatham Sts., Blue Island, Illinois.

▸ A close-coupled, portable electric motor and pump unit with dry suction lift of approximately 15 feet, designated as Model 4720, is now available. The unit consists of a stainless steel (Type 316) self-priming pump mounted directly on the shaft of a 1/4-hp., 1725-r.p.m. electric motor. It utilizes the neoprene impeller with 1/2-in. inlet and outlet ports designed to accommodate standard piping. Write Jabsco Pump Co., 2031 N. Lincoln St., Burbank, California, for *Bulletin 4720.*

▸ The Fiske Cryoscope is designed to measure freezing points to 0.001° C., on samples down to 0.2 ml. Time: one minute. Range is variable from +20° to −30° C.

Full details may be had from Advanced Instruments, Inc., Needham 92, Massachusetts.

▸ Bowen Engineering, Inc., North Branch, New Jersey, announces a new spray dryer, compactly designed for laboratory and small-lot production work. This new dryer, which has a greater drying capacity than the popular Bowen Table Model Spray Dryer, features a conical bottom drying chamber. The dryer also offers a choice of either nozzle atomization or centrifugal atomization or both.

▸ Now, Fisher Scientific Co., 717 Forbes St., Pittsburgh, 19, Pennsylvania, announces a major development in its line of 42 different clamps and holders: the jaws are hot-dipped in a tough vinyl plastisol. This coating replaces the rubber "sleeves" formerly used, and becomes a permanent and integral part of the clamp with exceptional gripping surface, better heat resistance, and superior aging qualities.

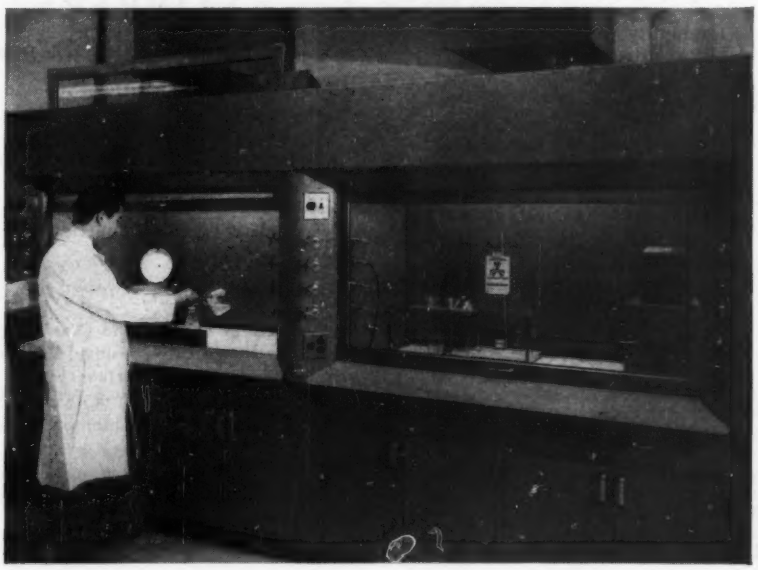
▸ Viewlex, Inc., 35-01 Queens Blvd., L.I.C., New York, introduces the new Project-O-Matic, 300 watt, motor fan cooled, automatic 2 × 2 Bantam slide projector. It is a beautifully designed, modern projector, all self-contained, with a built-in automatic slide changer and a slip-on aircraft luggage-type case.

▸ Automatic Projection Corp., 282 Seventh Ave., New York, N. Y. has developed a new model filmstrip and slide projector, the 500-watt Soundview "PhD" which is said to be the easiest operating, most positive, and quickest manual film advance mechanism in projector history. Another feature of great appeal to teachers is the ease and speed with which the filmstrip can be reviewed. The "perfect-framing" cam-lock can be released with a flick of the finger and the film "spun-back" to whatever picture is desired for review or study.

▸ The Swedish-crafted Nife Optical Pointer PF-4, designed for teaching and lecturing, is especially useful in conjunction with the use of slides or slide films. This new lightweight instrument will project a sharp image to a distance of 98 feet. Available from Nife, Inc., Copiague, L.I., New York.

▸ A new line of synthetic calcium silicates, called "Micro-Cel," has just been announced by the Celite Division of Johns-Manville, 22 E. 40th, St., New York 16, N. Y. Produced by the chemical combination of lime and diatomaceous silica, Micro-Cel is a powder available in specific grades which offer wide range of physical properties.

According to Johns-Manville Research, where these synthetic calcium silicates were developed, Micro-Cel provides a combination of properties which may hold the key to lower costs and improved prod-



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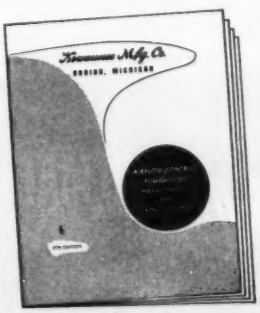
KEWAUNEE AIRFLOW FUME HOODS



- Scientifically designed for maximum protection of personnel working with radioactive or toxic materials.
- Aerodynamically efficient design permits substantially lower face velocities—⅓ to ½ less than conventional hoods.
- Constant volume exhaust with sash up or down.
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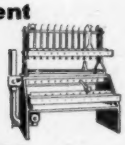
—Precision is the only manufacturer of a complete line of research laboratory equipment. Some 1500 items are quality-made by Precision for accuracy and dependability in the laboratory. Precision equipment includes:

Kjeldahl Equipment

Standard models and custom set-ups for every distillation and digestion need. Kjeldahl Extraction Rack illustrated.



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A complete line of "tools" and accessories for the laboratory. Sero-Utility Bath, at right, can be used as either a serological or utility bath.

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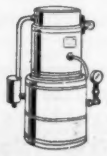
For processing or laboratory use. Recommended for use even with the hardest raw water. Electric, gas or steam heated. Automatically controlled.



Flash Point Testers

Cleveland type shown. Meets applicable A.S.T.M. and A.A.F. specifications.

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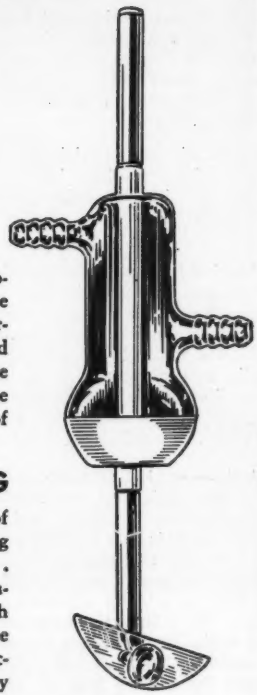

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Manufactured in a variety of styles to meet every laboratory need, Wilmad Precision Bore Stirrers are the ultimate in glassware craftsmanship. Rods and bearings fit to a closer tolerance than was ever believed possible. All stirrers, bearings, rods and blades are interchangeable and we stock them in a complete line of Standard Taper and Spherical Joints for all sizes of flasks.

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Available in Pyrex Brand Glass, Vycor and most of the electronic glasses, Wilmad Precision Bore Tubing is manufactured in various shapes and sizes . . . square, rectangular and tapered. Unbelievably accurate and uniform, this tubing can be supplied with I.D. tolerance down to ± .0002". O.D. can be ground to your specifications. A rigid 100% inspection of all our products eliminates rejects before they reach you.

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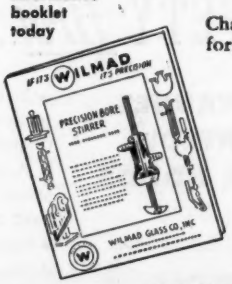

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Characteristic Wilmad precision maintains constant uniformity in our capillary tubing. Available in a range down to 0.4 mm I.D. and 1¾ mm O.D., this tubing reflects the craftsmanship which typifies every Wilmad product. This capillary tubing is particularly suitable for a multitude of uses in the pharmaceutical and biological fields such as: for blood coagulating and clot retraction time studies; micro dropper; sediment transfers to micro slides; hemoglobin drop test; removing supernatant fluids from centrifugal specimens, etc.

SPECIALISTS IN RESEARCH LABORATORY GLASSWARE

Jewel-like precision in laboratory glassware

CHEMICAL LABORATORY GLASSWARE

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ucts in many process formulations.

▸ Precision Scientific Co., 3737 W. Cortland St., Chicago 47, Illinois, has redesigned the Senior Model Ionograph, an analytical instrument utilizing electromigration of ions on wet filter paper in simple fractionations, mobility determinations, and reaction site studies.

▸ A new-type refrigerator that will maintain lower temperatures than any previous apparatus has been developed at Arthur D. Little, Inc., 30 Memorial Dr., Cambridge, Massachusetts. The temperature produced in the machine—approximately 500 degrees colder than those of the refrigerator in your kitchen—come to within a fraction of a degree of the coldest temperature that scientists believe can ever exist. There are no moving parts or flowing fluids in this cooling system. It uses, instead, a plastic capsule three inches long, containing a special chemical salt as the refrigerant. Operation of the refrigerator is controlled entirely by external magnetic fields.

NEW LITERATURE

● Consolidated Engineering Corp., 300 N. Sierra Madre Villa, Pasadena 15, California, has issued a new general catalogue, *Analytical and Control Instruments*. Another bulletin, *Process Refractometer* by the same company describes this instrument for monitoring and control in chemical and petroleum processes.

● Bulletin 100-D, *Index of Literature*, is a compilation of Honeywell information on instrumentation available from Minneapolis-Honeywell Regulator Co., Wayne and Windrim Aves., Philadelphia 44, Pennsylvania.

● Allied Radio Corporation, 100 N. Western Ave., Chicago 80, Illinois, has released its new 1956 catalogue (No. 150), featuring an unusually large selection of radio, television, and electronic parts and equipment for use in schools, classrooms, laboratories, and shops.

● *Facts About Titanium* contains a list of the commonly available titanium alloys and their compositions, forming and welding methods, heat treatment and machining information, as well as current and projected prices and other pertinent data. A brief comparison of titanium properties with those of a stainless steel and aluminum alloy is also included. Inquiries should be addressed to Arthur D. Little, Inc., Mechanical Engineering Division, 30 Memorial Dr., Cambridge 42, Massachusetts.

● A new publication, *Measurement of Vibration*, has been made available by the General Radio Co. This booklet, consisting of 64 pages, covers the meaning of vibration terms, description of vibration measuring instruments, procedures, typical examples, and interpretation of results. A short section is devoted to the human response to mechanical vibration. Copies are available from the General Radio Co., 275 Massachusetts Ave., Cambridge 39, Massachusetts.

● Sigma Chemical Co., 4648 Easton Ave., St. Louis 13, Missouri, announces publication of *Fall 1955 Biochemical and Organic Preparations*.

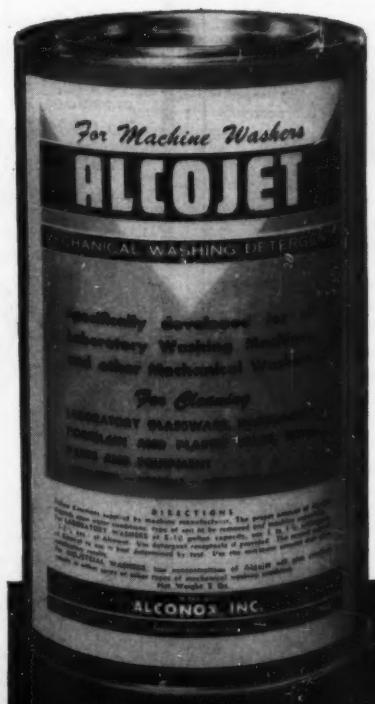
● A new edition of *What's New for the Laboratory*, 24th in the series, has just been announced by the Scientific Glass Apparatus Co., Inc., Bloomfield, New Jersey.

● A new price list shows availability for the first time of two new products: (1) Analytical Grade Chromatographic Alumina, and (2) Anion Exchange Resins which have been treated with an indicating dye to change color reversibly in going from the hydroxide to the other ionic forms. In addition, the *Price List "L"* includes current information on analytical grade anion and Cation Exchange resins prepared by purification of commercial-grade Dowes resins. Bio-Rad laboratories 800 Delaware St., Berkeley, California.

● A revised edition of the *Tempil Basic Guide to Ferrous Metallurgy*—in an $8^1/_2$-in. × 11-in. black and white version—is now available. This chart provides a handy reference source for the engineer, metallurgist, and skilled worker, and has proved to be an excellent teaching aid in fundamental courses on metallurgy. Available from Tempil® Corp., 132 W. 22nd St., New York 11, N. Y.

● General Biochemicals, Inc., 11 Laboratory Pk., Chagrin Falls, Ohio, is offering a new bulletin entitled, *Biological Test Diets* listing a wide range of prepared diets for the feeding of experimental animals. This little handbook is a ready reference for nutritional investigators engaged in biological research. Complete formula information and prices are given on a wide range of ready-to-use test diets. Various vitamin-, mineral-,

Only ALCOJET gives you the Big Difference in lab machine detergents



Yes, we're bragging—and understandably so; because we back our claim with the unconditional guarantee that if ALCOJET is not the finest machine detergent you have ever used, please return the empty box for a full cash refund.

If you use a machine washer to clean laboratory glassware, Porcelain, Metal or Plastic equipment use ALCOJET, the detergent specifically designed to prevent streaking, spotting or film residues.

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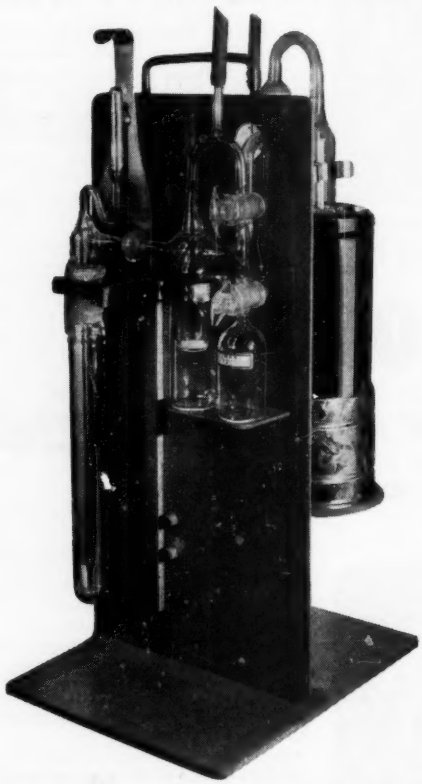
New DISTILLATION TRAIN

a vacuum distillation train in a single compact unit



A low temperature trap supplied with a Dewar, and a 20 mm fritted disk manostat. A new compact design. The manometer has a mirror metric scale, all mounted conveniently on a single base. Occupies a space 12″ square, 18″ high.

- **CONVENIENT** *Distillation Train ready for use at all times.*
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- **MANOMETER** *Air Trap design of Manometer allows easy filling. Adjustable mirror scale eliminates parallax in reading.*

This distillation train is furnished with a gray crackle finished base and chrome non-corrosive clips, also a handle, which is conveniently mounted for ease of carrying.

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No. CE-2314-M. WACO Separator. For 110 V. 60 cycle. CAST ALUMINUM HEAD. With removable tube holders for two 100 mm. and two 75 mm. test tubes (other selection is permitted).

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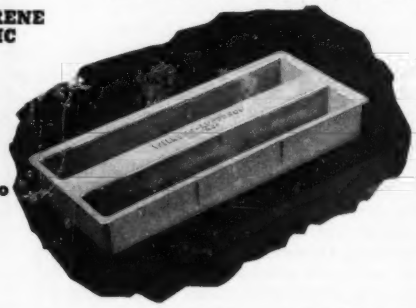

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● A 600% increase in the use of molybdenum in catalysts over the past two years is reported in *Molybdenum Catalysts for Industrial Processes*, a 24-page booklet just published by Climax Molybdenum Co., Dept. L, 500 Fifth Ave., New York 36, N. Y.

● *Techniques*, a new publication of Barnes Engineering Co., 30 Commerce Rd., Stamford, Connecticut, features news of developments in Automation Equipment, Infrared Components and Systems, and Process Control Instrumentation.

● Two new catalogues of technical reports available from the Government, one on electroplating and polishing and the other on photochemistry and photoelectricity, have been compiled by the Office of Technical Services, U. S. Department of Commerce. Price of the catalogues is 10 cents each. They are CTR-159, *Electroplating and Polishing*, and CTR-311, *Photochemistry and Photoelectricity* (excluding photography), and may be ordered from OTS.

● The first comprehensive review of industrial applications of molybdenum chemicals has been published by the American Chemical Society and is now available in reprint form from Climax Molybdenum Co., Dept. L, 500 Fifth Ave., New York 36, N. Y.

Comprising seven different papers, this survey details molybdenum's wide use in diverse chemical fields, and points to new industrial applications resulting from the present increased tempo of molybdenum research. The papers were originally presented under the sponsorship of the American Chemical Society's Division of Industrial and Engineering Chemistry.

● *L & N File Publications* is an index to Leeds and Northrup literature on automatic controls, measuring instruments, and various manufacturing processes. Ask for Booklet *ENT 1*, Leeds and Northrup Co., 4901 Stenton Ave., Philadelphia 44, Pennsylvania.

● An informational folder on Trona soda ash has been prepared by American Potash & Chemical Corp., for use in such industries as glass, mining, and metallurgy, soaps and detergents, plywood and adhesives, and chemical processing. Copies of the bulletin can be obtained by writing American Potash & Chemical Corp., 3030 W. Sixth St., Los Angeles 54, California.

● Precision Scientific Co., 3737 W. Cortland St., Chicago 47, Illinois, has published *Bulletin 912* on their "Midget" Water Still, a laboratory still especially designed for small-volume but high-purity requirements.

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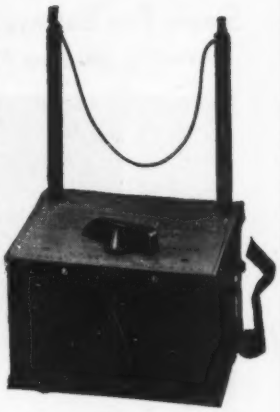

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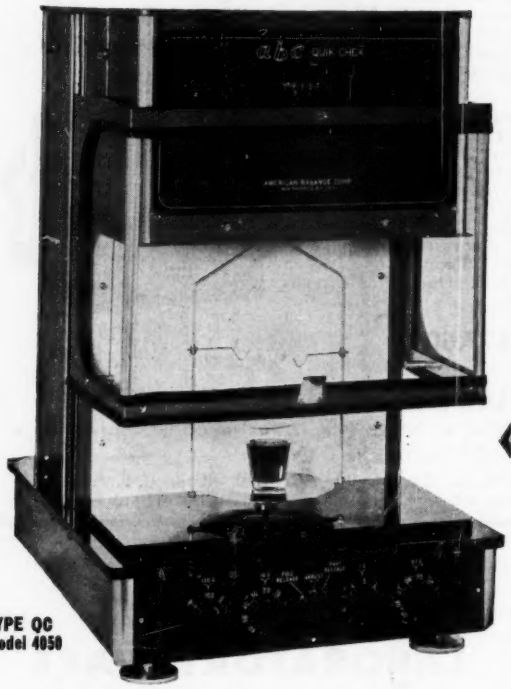

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References

(1) Ind. Eng. Chem. 25-653 (June, 1933)
(2) Ind. Eng. Chem. 25-1112 (Oct., 1933)
(3) National Bureau of Standards Journal of Research 12-241 (Feb. 1934, R.P. No. 649)

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● New 12-page *Burrell Booklet 83* describes the Kromo-Tog, a new self-contained instrument for the analysis of gases and liquids by gas chromatography.

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Burrell Corp., pioneers in gas chromatography, offer the new *Booklet 83* free on request to the company at 2223 Fifth Ave., Pittsburgh 19, Pennsylvania.

● The Photovolt Corp., 95 Madison Ave., New York 16, N. Y., offers a new *Bulletin #118* on a battery-operated pH meter Model 125.

● The latest type of infrared detectors used as sensing elements in radiometer, pyrometers, infrared spectrometers, and other infrared instruments are described in a new bulletin called *optiTherm Infrared Detectors*. Published by Barnes Engineering Co., 30 Commerce Rd., Stamford, Connecticut, the bulletin describes the characteristics, construction, circuitry, and uses of these high-speed thermistor-type sensing elements.

● Latest issue of *Lanco Apparatus News* (Volume 7, No. 1) has been published by Arthur S. LaPine & Company, 6001 S. Knox Ave., Chicago 29, Illinois. Featured items are a new model polyethylene sink trap, flash-evaporator, separatory funnels and burets with Teflon plugs, and a "do-it-yourself" water bath with a new electronic relay.

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★ A promising future for the small gas turbine was predicted by Mr. P. L. Ward of the Solar Aircraft Co., in a paper presented to the National Meeting of the American Institute of Chemical Engineers at Lake Placid. The industrial use of small gas turbines is advancing, he stated, in spite of its high fuel consumption because of substantially lower maintenance costs. At the same time, he pointed out the areas of greatest use. The small gas turbine has been selected where weight is important, such as in aircraft, or as portable fire-fighting pumps. Reliable starting ability in cold weather is another reason for increasing use of this machine. Oil companies are finding the small gas turbine useful in exploration, both in frigid Canada where the exhaust heat is useful, and in arid deserts where water is more expensive than fuel. Where low-cost fuel is available the gas turbine is readily accepted.

★ A plan analogous to the workmen's compensation act has been advocated to cover public liabilities in nuclear reactor operations.

The suggestion was made by William M. Cousins, Jr., assistant director of Armour Research Foundation of Illinois Institute of Technology, at the Atomic Industrial Forum's annual meeting.

Cousins recommended the passage of an "atomic compensation act" which would provide for fixed damage payments to the public and a fixed limit of liability for companies.

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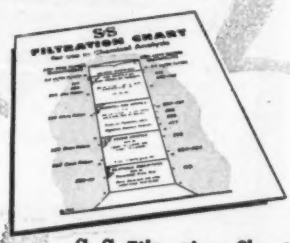

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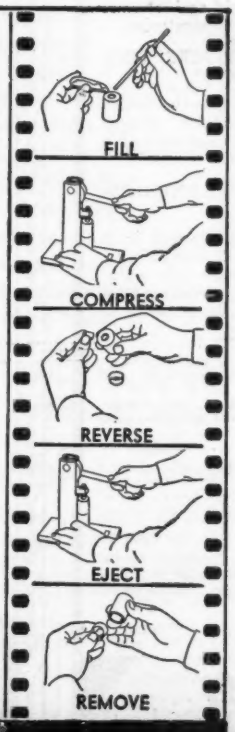

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Cousins described many of the safety precautions taken in installing the nation's first nuclear reactor specifically for industrial research at Armour Research Foundation's facilities in the heart of Chicago. The reactor, which will be completed early in 1956, also is the first to be constructed in a highly populated area since the development of Fermi's original reactor in 1941. Cousins estimated that some 11,000 persons live within a radius of 1500 feet of the site of Armour's reactor. Cousins praised the press and the Atomic Energy commission for their assistance in quieting the fears of the public.

★ *Peaceful Uses of Atomic Energy:* Secretary-General Dag Hammarskjold announced the forthcoming publication by the United Nations of the Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, held in Geneva in August, 1955.

The Proceedings, which will be published in 16 volumes of approximately 500 pages each, will constitute the complete, unabridged record of the Conference, and comprise all papers, whether presented orally or in written form at the Conference, together with a record of the discussions concerning each paper.

These Geneva papers will be published by the United Nations in several languages; the English edition will be available in the beginning of 1956, the other at a later date still to be determined.

The publication, in full, of the Geneva papers is considered unique in that it will be the only publication which will make available, in their entirety, the more than 1,000 scientific papers submitted at the Conference by over 30 countries and international agencies, and will constitute the only complete record of the Conference, at which approximately 1,200 scientists from 72 countries participated.

Any of the individual scientific papers, in mimeographed form, may be purchased at 25 cents each by designating the author and title, from the United Nations Bookshop.

The following are the tentative titles of the 16 volumes: Volume 1, "The World's Requirements for Energy; The Role of Nuclear Power." Volume 2, "Physics; Research Reactors." Volume 3, "Power Reactors." Volume 4, "Cross-Sections Important to Reactor Design." Volume 5, "Physics of Reactor Design." Volume 6, "Geology of Uranium and Thorium." Volume 7, "Nuclear Chemistry and the Effects of Irradiation." Volume 8, "Production Technology of the Materials Used for Nuclear Energy." Volume 9, "Reactor Technology and Chemical Processing." Volume 10, "Radioactive Isotopes and Nuclear Radiations in Medicine." Volume 11, "Biological Effects of Radiation." Volume 12, "Radioactive Isotopes and Ionizing Radiations in Agriculture, Physiology, and Biochemistry." Volume 13, "Legal, Administrative, Health and Safety Aspects of Large Scale Use of Nuclear Energy." Volume 14, "General Aspects of the Use of Radioactive Isotopes; Dosimetry." Volume 15, "Applications of Radioactive Isotopes and Fission Products in Research and Industry. Volume 16, "Record of the Conference.

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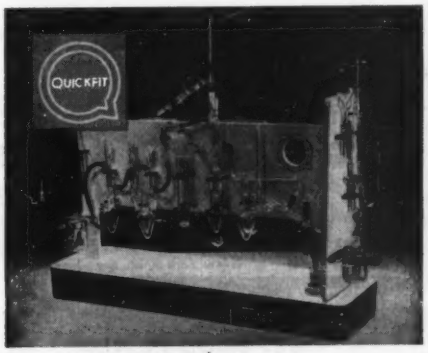

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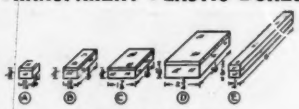

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(3) In the performance of amperometric titrations.

(4) For instructional purposes in educational institutions where the 315 mm. long, readily visible scale and the simplicity of design make the Model III Polarograph ideal for demonstrations and illustration of the basic circuit employed in Polarographs.

Essentially the Model III provides facilities for the incremental application of voltage across the dropping mercury electrode cell and for indicating the resultant current passing through the cell. The cell current is measured by a highly sensitive galvanometer from which a line light image is transmitted, through a mirror system, to a translucent scale located above the instrument panel. The scale is double graduated from −150 to +150 mm. with zero center in red at top and from zero to +300 mm. in black at the bottom. The scale is 31.5 cm. long, with circular curvature, to eliminate tangent error. Each graduation is extended 15 mm. at left for zero adjustment. A continuous selection of bridge voltage from 0 to 3 volts is provided, and the selection of output voltage is by rotation of a single dial, this dial reading direct in millivolts per span volt. Current is calculated simply by multiplying scale reading by multiplier reading by sensitivity coefficient of galvanometer. To adjust galvanometer sensitivity a ten position Ayrton galvanometer shunt is provided. Galvanometer sensitivity is approximately 0.005 microamperes/mm. and galvanometer shunt ratios are from 1:1 to 1000:1. A three position toggle switch permits that the sense of the galvanometer scale remain unchanged regardless of cell current direction or polarity of the dropping electrode.

A ten turn helical potentiometer serves both for upscale and downscale compensation and for adjustment of the galvanometer zero position.

Another potentiometer incorporating a power switch serves to select the desired voltage across the bridge. A panel mounted voltmeter accurate to 1.0% of full scale indicates the voltage established.

The instrument is mounted on a cast aluminum base and enclosed in a sheet metal housing provided with a hinged top and finished in black enamel. All controls are mounted on a polished aluminum panel.

S-29290 POLAROGRAPH—Manual, Indicating, Model III, Sargent. Complete with three No. S-30858 dry cells, one No. S-29304-A galvanometer lamp, one set No. P.N. 1995 cell lead wires, one No. P.N. 2067 calibrating resistor plug, 250,000 ohm, and cord and plug for connection to standard outlets. For operation from 115 volt 50 or 60 cycle circuits.....**$390.00**

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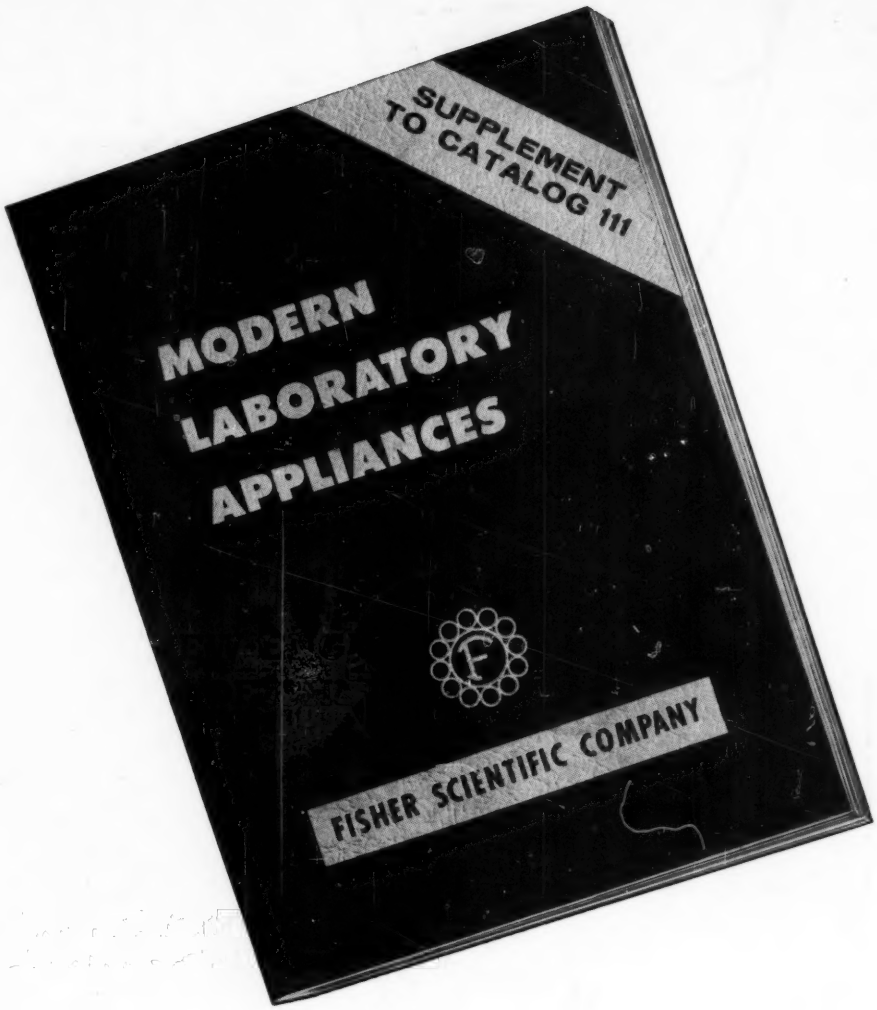

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